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DETERMINATION OF PHYSICAL AND CHEMICAL STRUCTURE OF
NEW HIGH-TEMPERATURE POLYMERS

K. A. Boni

Battelle Memorial Institute

TECHNICAL REPORT AFML-TR-69-292, Part I

November 1969

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DETERMINATION OF PHYSICAL AND CHEMICAL STRUCTURES
OF NEW HIGH-TEMPERATURE POLYMERS

by

K. A. Boni

Battelle Memorial Institute
Columbus Laboratories

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FOREWORD

This report was prepared by the Columbus Laboratories of Battelle Memorial Institute under USAF Contract F33615-69-C-1095. The contract was initiated under Project No. 7340, "Nonmetallic and Composite Materials", Task No. 734004, "New Organic and Inorganic Polymers". It is administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. T. E. Helminiak as project scientist.

This report covers work conducted from October 1, 1968 to August 31, 1969. The manuscript was released by the author in October 1969 for publication.

This report was prepared by Dr. Kenneth A. Boni, Principal Investigator. Structural analyses were performed by Mr. R. J. Jakobsen (IR), Dr. R. L. Foltz (Mass Spectrometry), and Mr. T. F. Page (NMR). Thermal analysis was performed by Mr. R. W. Pfeil. The other characterization was performed by Mr. Daniel Nemzer, Mr. G. P. Nance, Mr. K. C. Price, Mrs. M. C. Hall, Mrs. C. S. Pierce, and Mr. T. Lyons. The contract was administered by Mr. E. R. Mueller of the Organic and Polymer Characterization Division.

This technical report has been reviewed and is approved.

WILLIAM E. GIBBS
Chief, Polymer Branch
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ABSTRACT

Several samples of a silicon-nitrogen elastomer were characterized. Characterization included structure analysis (elemental composition, IR, and NMR), solubility, solution viscosity, thermal properties (TGA and subambient DTA), and molecular weight (M_n , M_w , GPC distribution). The samples appeared to have the expected structure, i. e., linear polymers, began to volatilize appreciably above 500 C, had a Tg at -27 C, and a broad molecular-weight distribution with M_w as high as 250,000.

Several samples of the perfluoroalkyl bibenzoxazole polymers were examined. Considerable effort was directed toward determination of the molecular weight of both perfluorosebacate and perfluoroalkyl ether-linked polymers. In addition, solubility, thermal stability and subambient DTA of the perfluoroalkyl ether-linked polymers (elastomers) were investigated.

Samples of the aromatic heterocyclic-ladder type were studied. Mass-spectral identification of the volatiles produced by programmed heating of an incompletely cyclized sample indicated that decarboxylation occurs within the same temperature range as does the cyclization.

The product obtained by heating 1-carboxy-2-chloroferrocene was studied. The reaction mechanism was investigated by structural analysis of the product and analysis of the volatiles produced during reaction.

Several samples of polyspirocyclobutane polymers were characterized. Characterization includes structural analysis, solubility, and thermal properties.

The approach to solvent search was examined in the light of recent literature. It was concluded that division of the solubility parameter into electrostatic and covalent contributions would describe solvent properties pertinent to solution formation. This was supported by examination of solubility data for several polymers.

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INTRODUCTION

In recent years, the Air Force has been faced with a growing need for new materials for use in extreme environments. As a result, a sizable polymer synthesis program has been supported. In general, an initial screening for probable structure, possible applications, and upper service temperature is performed as part of these synthesis programs. However, much greater benefit from the synthesis programs is possible if all polymeric products are thoroughly characterized by a single laboratory whose primary interest is polymer characterization. Accumulation of characterization data by one laboratory eventually leads to development of structure-property correlations which can be used to direct synthesis programs to more fruitful approaches to useful polymers. Additional incentive for characterization of synthesis products by characterization specialists is to provide impartial and rapid recognition of the potential of candidate materials. This report is a description of work performed at Battelle on such a characterization program.

In general, characterization includes structure identification, solvent search, thermal properties, solution viscosity, and molecular weight. Infrared (IR) and nuclear magnetic resonance (NMR) spectra, and elemental analysis were used for structure identification. Since determination of the primary structure of samples was part of the synthesis programs, only the general features of the structure were examined. Solubility and swelling behavior of candidate materials was predicted from examination of mixtures of the materials with solvents which provided systematic variation of the electrostatic and covalent solubility parameters.

Differential thermal analysis (DTA) was used to measure the magnitude and temperature range of any thermal transitions produced during programmed temperature rise. An indication of the thermal stability of the material was obtained by thermogravimetric analysis (TGA). In a few cases, the TGA data were supplemented by mass spectral identification of thermal-fragmentation products to provide insight into the fragmentation mechanism.

Solution-viscosity measurements provided an estimate of sample molecular weight. Generally, the specific viscosity was determined at several concentrations to avoid the possibility of not observing polyelectrolyte effects. When more precise molecular weights were desired, osmometric techniques were used to provide number-average molecular weight (M_n). Also, the molecular weight distribution was determined by gel-permeation chromatography (GPC) when suitable solvents were available.

II

EQUIPMENT AND PROCEDURES

Details of the equipment and characterization techniques used in this program not referred to in this section have been reported previously^{(1,2)*}.

Light Scattering

All light-scattering-intensity measurements are made with the sophica light-scattering instrument. The alignment of the instrument and the uniformity of the scattering cells were checked by use of a 60:40 water-ethanol solution of fluorescein. Constancy to better than 1 percent of the product of the fluroescing intensity and the sine of the angle of observation was obtained. By use of a 10 mV Honeywell Brown Elektronik recorder to observe the scattering intensity, the intensity readings were accurate to ± 0.2 percent.

A Phoenix Precision differential refractometer was used for determination of the refractive index increment of solutions, i. e., dn/dc . The cell chamber was insulated and the cap supplied with the instrument replaced by a 3/4-inch aluminum cap to permit operation at elevated temperature. Temperature control in the chamber after these modifications was better than ± 0.1 C.

Differential Thermal Analysis (DTA)

In addition to the Model 12AC Stone DTA described in a previous report⁽¹⁾, Battelle has recently acquired a new Stone DTA. This instrument includes a 202 series Stone recorder-controller, a model H-5 subambient and a model JP-202 elevated-temperature platform, furnaces and cells, which permit the following:

- (1) Continuously variable heating rates from 0.5 C per minute to 50 C per minute, with infinitely variable upper and lower temperature limits and five automatic switch modes including standby, hold, heat, cool, and cycle
- (2) Infinitely variable ΔT sensitivity with a maximum sensitivity of 0.002 C per chart division
- (3) Choice of eight temperature scales from -150 C to +160 C and from 0.0 C to +1600 C
- (4) The data output is recorded on a three-channel strip-chart recorder which displays temperature, ΔT , and the first derivative of ΔT
- (5) Normal sample pressure can be controlled from 1×10^{-2} torr to 100 psia with the standard platform (acquisition of a special

*Superscript numbers denote references given at the end of this report.

holder would extend this range, if required, from 1×10^{-6} torr to 3000 psia)

- (6) Use of a high-temperature furnace and cell to extend the normal temperature range from 1100 C to +1600 C by simple plug-in of the high temperature cell.

III

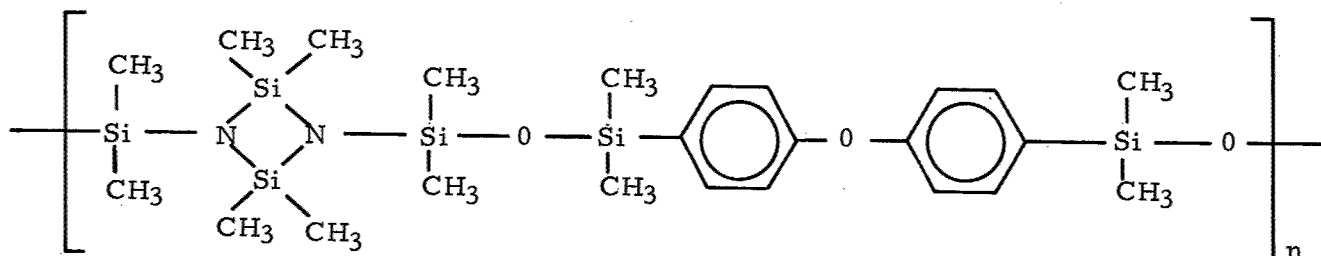
RESULTS AND DISCUSSION

Silicon-Nitrogen Polymers

Initial characterization results on samples of the polymeric products of the thermally induced condensation of N, N'-bis(dimethylaminodimethylsilyl)tetramethylcyclodisilazane with bis(p-dimethylhydroxysilylphenyl) ether suggested that they have elastomeric properties and good thermal stability.⁽²⁾ However, rapid crosslinking of the product during storage produced a nonmillable gel. Recent work by Breed et al.,⁽³⁾ indicates that the rate of crosslinking is greatly reduced when the condensation product is "end-capped" with bis(trimethylsilyl) acetamide to produce trimethylsilyl end groups. They report that the inherent viscosity and solubility of several end-capped samples remained unchanged after storage for 30 days.

Three samples of end-capped polymers were submitted to Battelle for characterization. One of these, labelled HR-109, was chosen as representative of these polymers and characterized as to structure, thermal properties, solubility, molecular weight, and molecular weight distribution. This sample plus the remaining two, labelled HR-111 and HR-112, were submitted to generate viscosity - molecular weight relations.

The infrared (IR) spectrum of sample HR-109 (see Figure 1) obtained by ArRo Laboratories, Incorporated, on a KBr smear is in good agreement with the proposed structure:



The bands at 1580 and 1500 cm^{-1} are consistent with a para disubstituted benzene, the 1115 cm^{-1} absorption with a phenyl-silicon bond, the 1260 cm^{-1} band with a methyl-silicon bond, the 1075 and 1020 bands with a siloxane, the bands at 1250 and 1020 with a diphenyl ether and the bands between 750 and 860 cm^{-1} with carbon-silicon absorptions. An X-ray analysis of bis(trimethylsilyl) tetramethylcyclodisilazane by Wheatley⁽⁴⁾ suggests that the methyl groups on the cyclodisilazane ring may not be equivalent. This could lead to four absorption bands in the 750-860 cm^{-1} region as observed by infrared spectroscopy (IR). According to Breed and Elliot⁽⁵⁾, the weak absorption at 950 cm^{-1} indicates that very little ring cleavage has occurred.

The nuclear magnetic resonance (NMR) spectrum of the sample in toluene (see Figure 2) was obtained as an additional check of the structure and as a means of identifying the source of the four bands in the 750-860 cm^{-1} region of the IR spectrum.

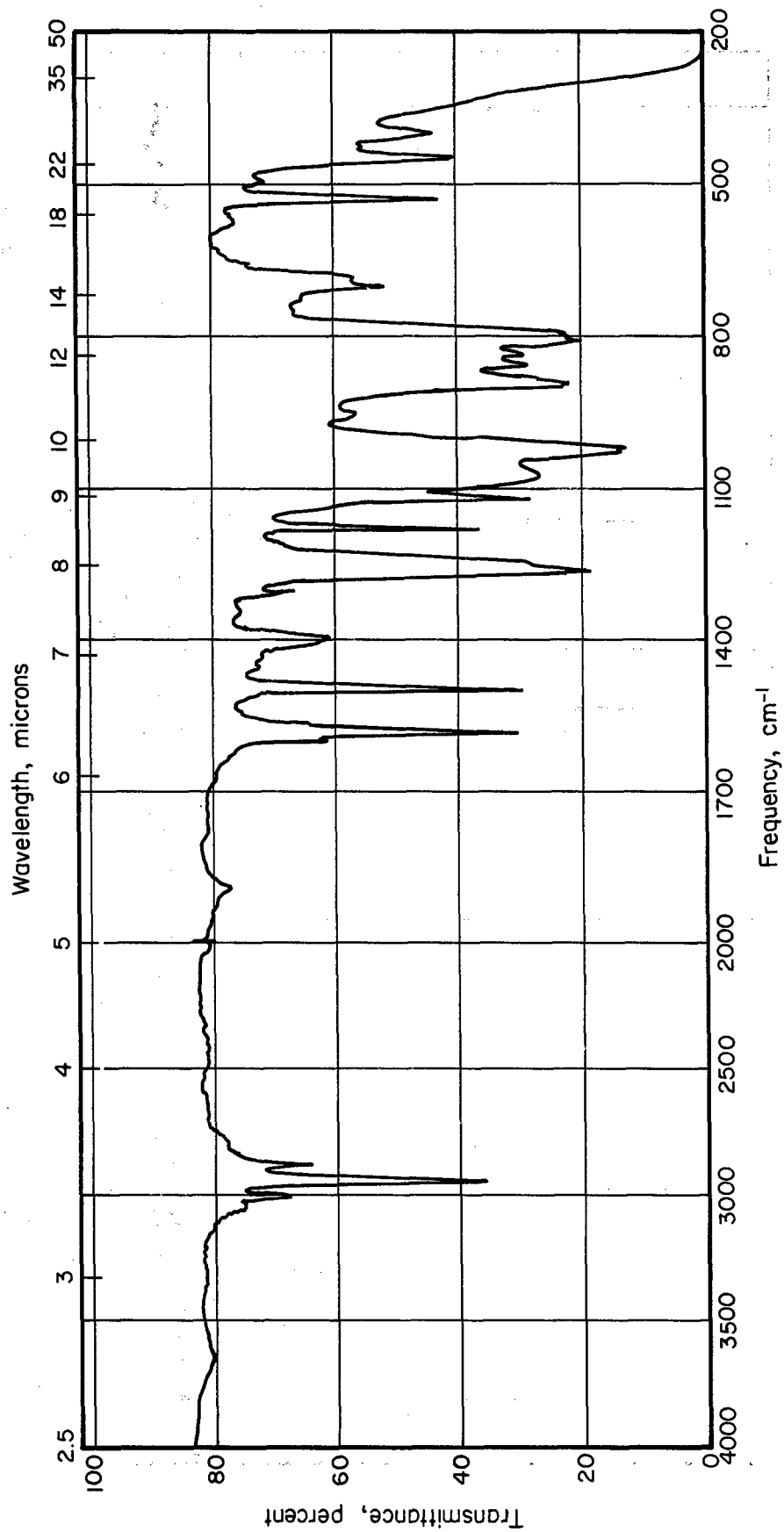


FIGURE 1. INFRARED SPECTRUM OF SILICON-NITROGEN POLYMER SAMPLE HR-109
KBR SMEAR

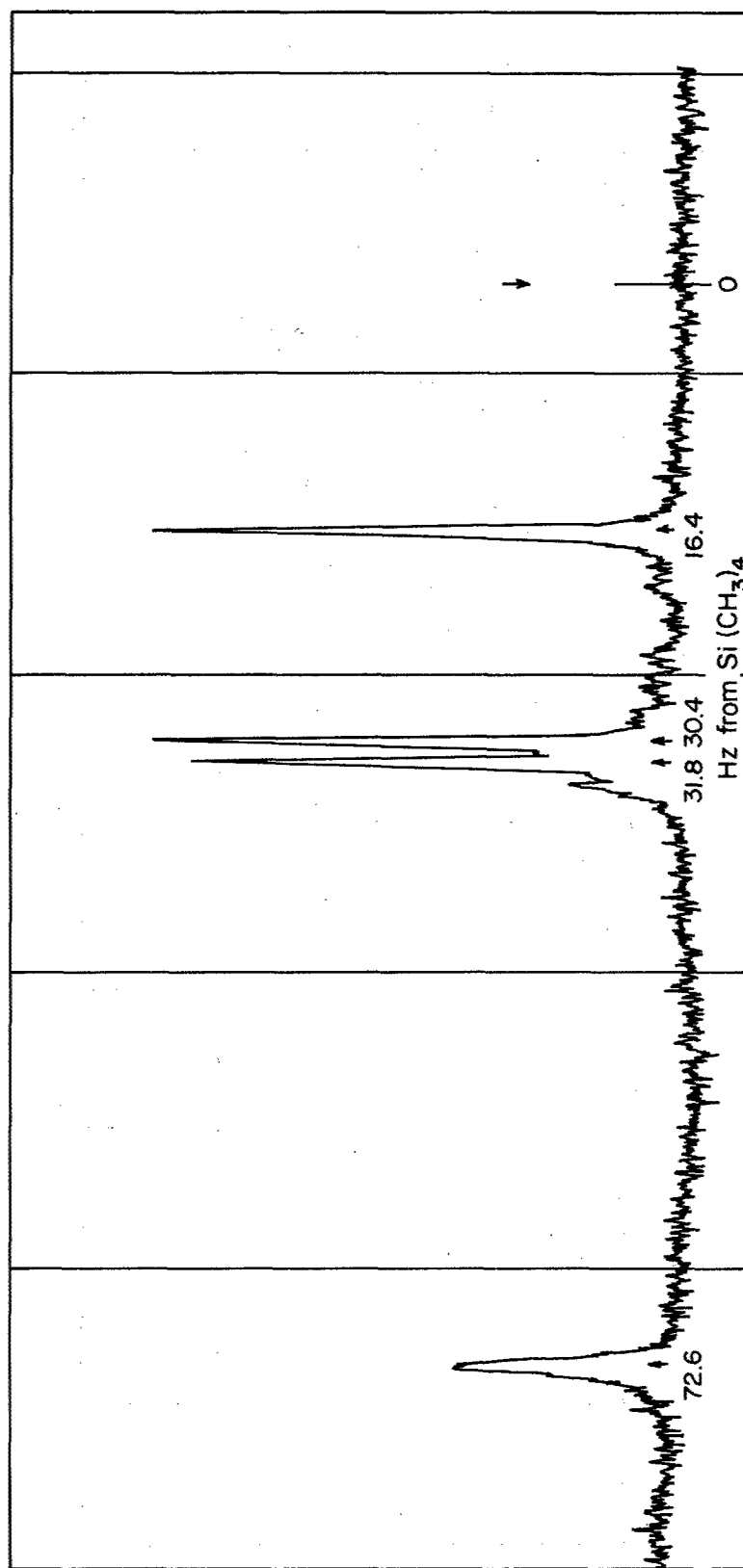


FIGURE 2. ^1H NMR SPECTRUM OF SILICON-NITROGEN POLYMER SAMPLE HR-109

While four distinct aliphatic proton resonances were observed, it appears that one of them arises from substantial residual dimethyl amine. NMR spectra of model compounds, kindly supplied by L. W. Breed, greatly aided this interpretation. Since para-disubstituted aromatic absorptions occur in the 750 to 850 cm^{-1} region of the IR spectrum, the extra band in this region of the spectrum is most probably produced by the para-disubstituted benzenes. Either the differences in bond length and electronic environment of the two methyl groups on the cyclodisilazane predicted by the X-ray measurements are too small to resolve or they exchange relatively rapidly with respect to the measurement period of IR and NMR.

The elemental analysis of sample HR-109, shown in Table I, is in good agreement with that calculated for the proposed structure, with the exception of the silicon content reported by Clark Microanalytical Laboratories. The consistency of the spectral data and the Spang Microanalytical Laboratory silicon analysis with the proposed structure suggests that some error was made in the Clark analysis.

TABLE I. ELEMENTAL ANALYSIS OF SILICON-NITROGEN
POLYMER SAMPLE HR-109

Element	Analysis, percent	
	Calculated	Observed
C	49.93	49.12(a)
H	7.69	7.61(a)
N	4.85	4.84(a)
Si	29.19	11.57(a), 30.46(b)
O	8.31	--

(a) Average of duplicate analysis by Clark Microanalytical Laboratory.

(b) Average of duplicate analysis by Spang Microanalytical Laboratory.

A solvent search was performed with this sample by the microscopic technique⁽¹⁾ using the solvent list developed to provide solvent-property variation based on division of the solubility parameter into electrostatic and covalent portions. It is clear from the solvent formulating map (Figure 3), that the sample will form greater than 0.1 percent solutions with solvents having a large range of properties. In addition, the lack of solubility in solvents with a high electrostatic solubility parameter indicates the intermolecular forces in solution are principally nonpolar.

The TGA thermogram of the "as-received" sample of HR-109 (Figure 4) shows that volatilization of the sample starts above 300 C. However, the magnitude of the weight loss between 300 and 500 C suggests that it may arise from loss of impurities rather than breakdown of the polymer into volatile fragments. Isothermal aging or analysis of the volatiles could be employed to determine the mechanism of this early weight loss. An attempt to identify the volatiles by use of the TGA-mass spectrometer (AEI MS-10) was unsuccessful. No appreciable volatiles attributable to decomposition fragments or trapped solvent were identified.

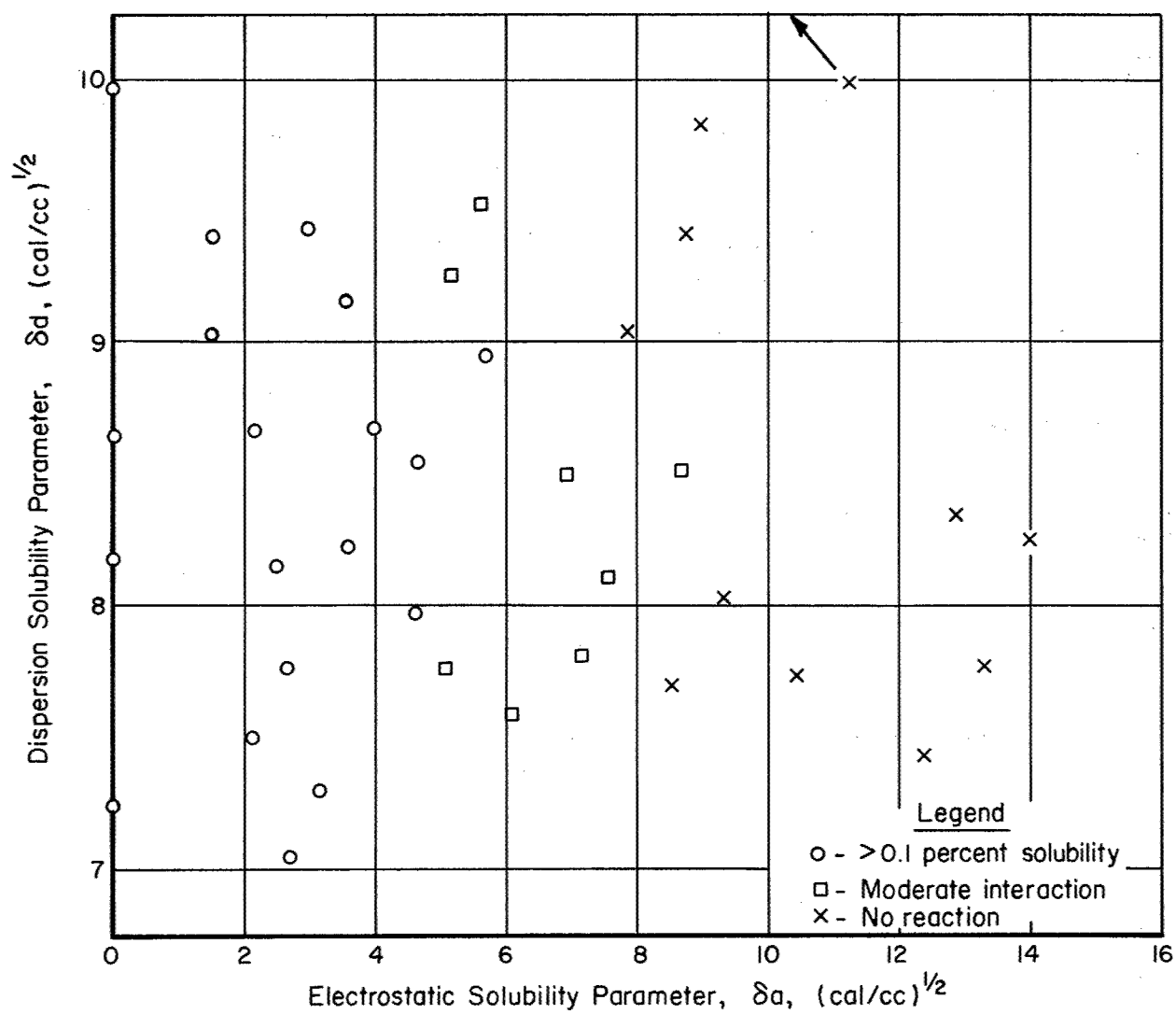


FIGURE 3. SOLVENT FORMULATING MAP FOR SILICON-NITROGEN POLYMER SAMPLE HR-109

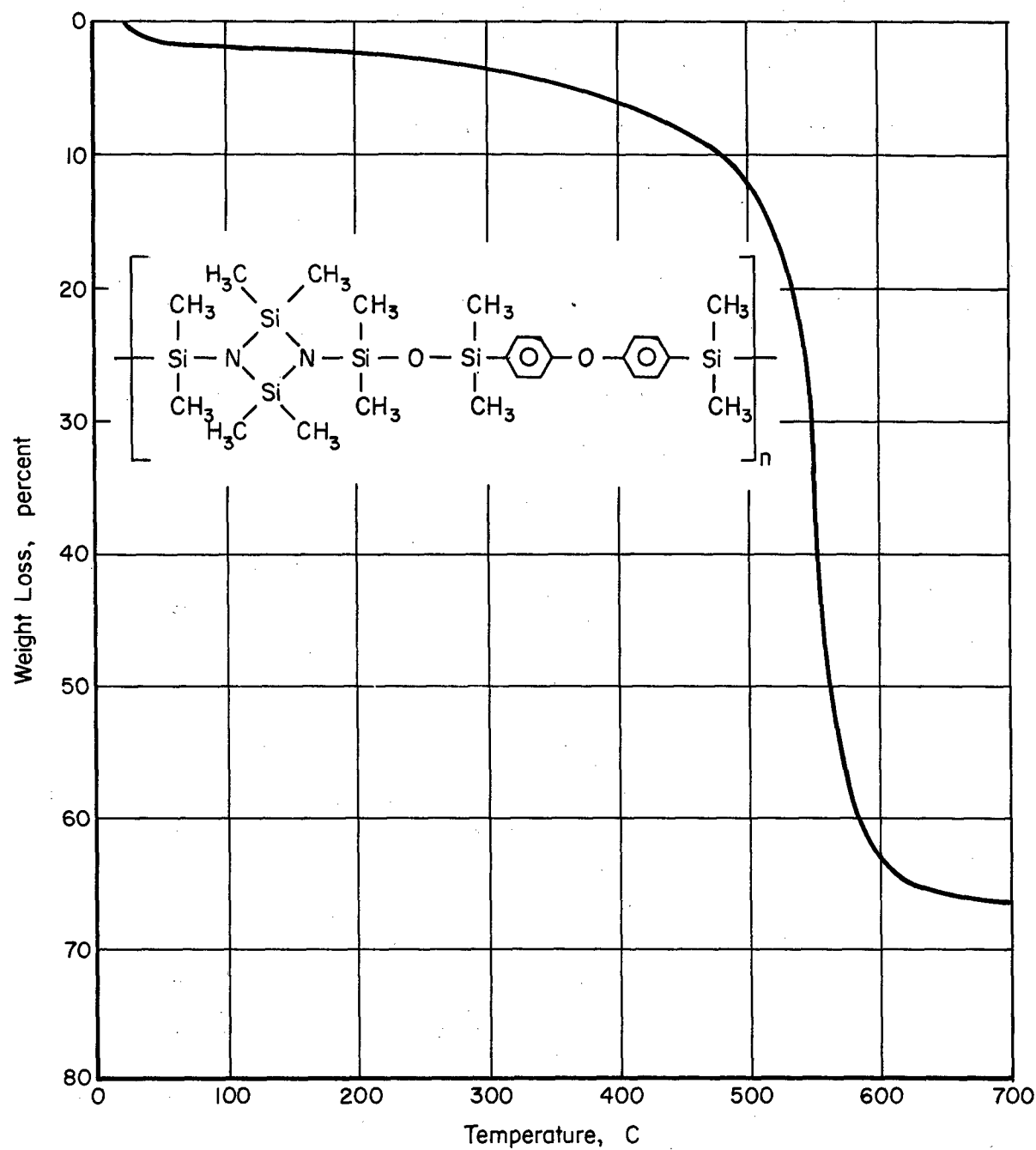


FIGURE 4. TGA THERMOGRAM OF SILICON-NITROGEN POLYMER
SAMPLE HR-109 AT 4C/MIN HEATING RATE AND
0.1 TORR USING A 14.54 MG SAMPLE

The TGA thermogram of Sample HR-105, a Si-N polymer previously characterized(2), is included in Figure 4 to illustrate the effect of end-capping on thermal stability. While the differences between the thermograms exceed experimental error (particularly between 300 and 500 C), the differences could reflect different molecular weight distributions or contamination. The magnitude of the differences suggests that the end-capping has not changed thermal stability significantly.

The glass-transition temperature of Sample HR-112 was determined on Battelle's subambient DTA (see "Equipment and Procedures" section for description). The thermogram (see Figure 5) indicates a glass transition at -27 C. This transition was confirmed by thermograms obtained with different amounts of sample.

Obviously, characterization of an impure polymer would result in development of erroneous structure-property relations. Since this sample had an amine odor when received, contamination with dimethylamine, a reaction by-product, was suspected. Such contamination could also be the source of the weight loss between 300 and 500 C observed by TGA. Freeze drying from benzene was investigated as a means for removing the volatile contamination. This technique was chosen because a relatively porous structure is maintained during evacuation.

The NMR spectrum and the TGA thermogram of the freeze-dried sample were obtained to assess whether the dimethylamine was completely removed. Ethanol-free chloroform was used in place of the toluene employed in the initial NMR analysis to avoid interference with the aromatic protons. The NMR spectrum indicated complete removal of dimethylamine and a structure consistent with the proposed structure. The proton resonances from the methyl groups on the cyclodisilazane were also equivalent in this solvent. In view of this NMR data, the presence of material which begins to volatilize at 150 C as indicated in the TGA thermogram of this sample (see Figure 6) is quite surprising. The marked difference in the TGA thermogram of this polymer produced by the freeze drying and the absence of benzene in the volatiles produced by heating the freeze-dried sample (TGA-mass spectrometer) suggests that additional reactions have occurred. This hypothesis is supported by the viscosity and gel permeation chromatographic analyses reported subsequently in this section.

In view of the potential of this polymer as a high-temperature elastomer, a means for rapidly and reliably estimating molecular weight of polymers of this structure is desired. Therefore, the intrinsic viscosities of all the submitted samples were measured with the intention of generating a viscosity - molecular weight relation. The intrinsic viscosities, determined in toluene at 30 C using semimicro Cannon Ubbelohde viscometers in conjunction with a Hewlett-Packard "Autoviscometer", are listed in Table II along with the inherent viscosities included in the transmittal information. The limited range of viscosity covered by these samples precludes their use for generating a reliable viscosity - molecular weight relation.

The molecular-weight distribution of all the silicon-nitrogen polymer samples was examined by gel permeation chromatography (GPC). The chromatograms (see Figures 7-10) were obtained from 4.4×10^{-3} g/ml tetrahydrofuran solutions using the Waters gel-permeation chromatograph. The most surprising feature is the marked increase in the amount of high-molecular-weight molecules produced by freeze drying Sample HR-109 from a benzene solution. Also, it is interesting to note that all the samples have molecules which are retained on the GPC columns longer than the 4×10^5 molecular-weight polystyrene standard. Also, all traces have a shoulder with a

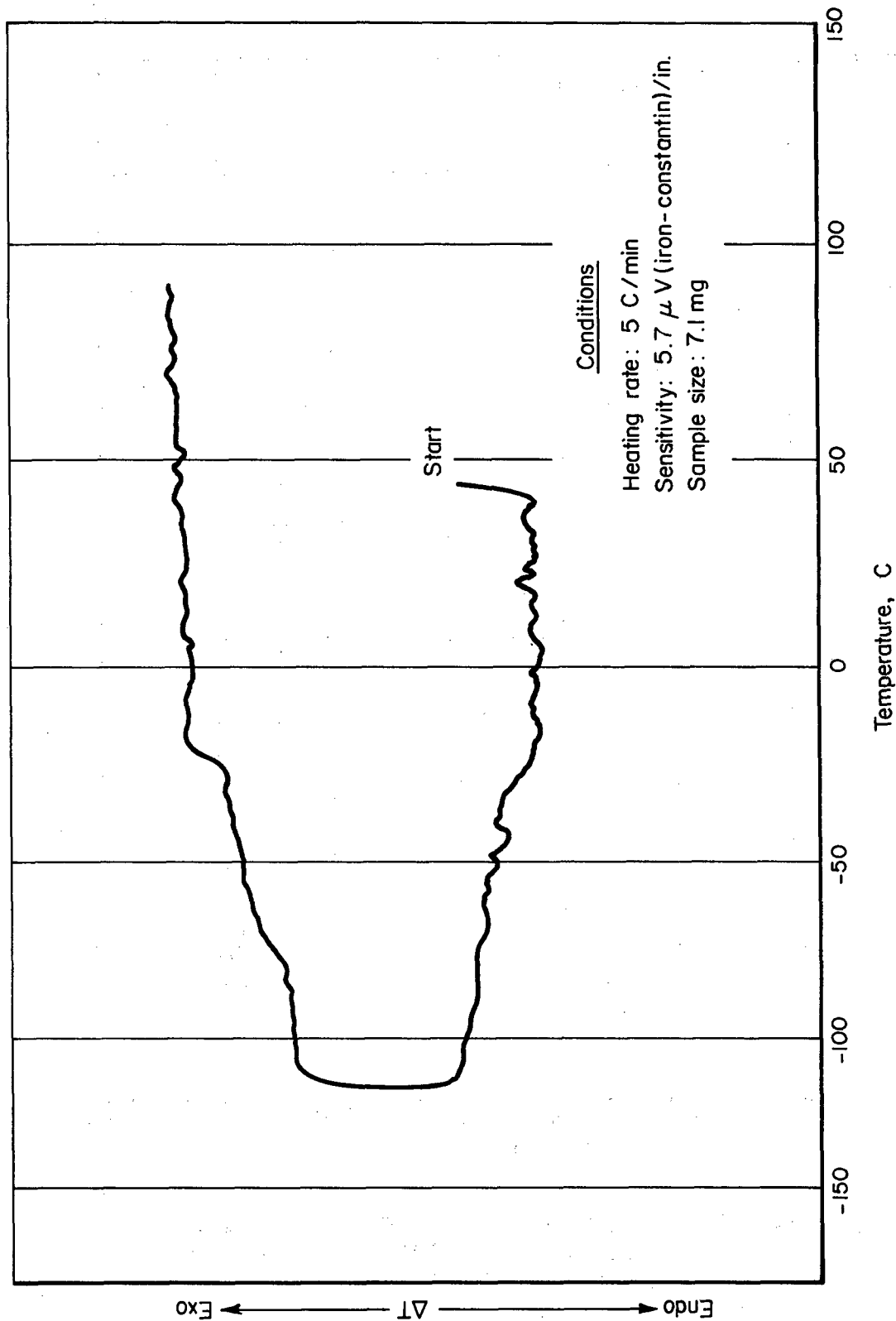


FIGURE 5. SUBAMBIENT DTA THERMOGRAM OF SILICON-NITROGEN POLYMER
SAMPLE HR-112

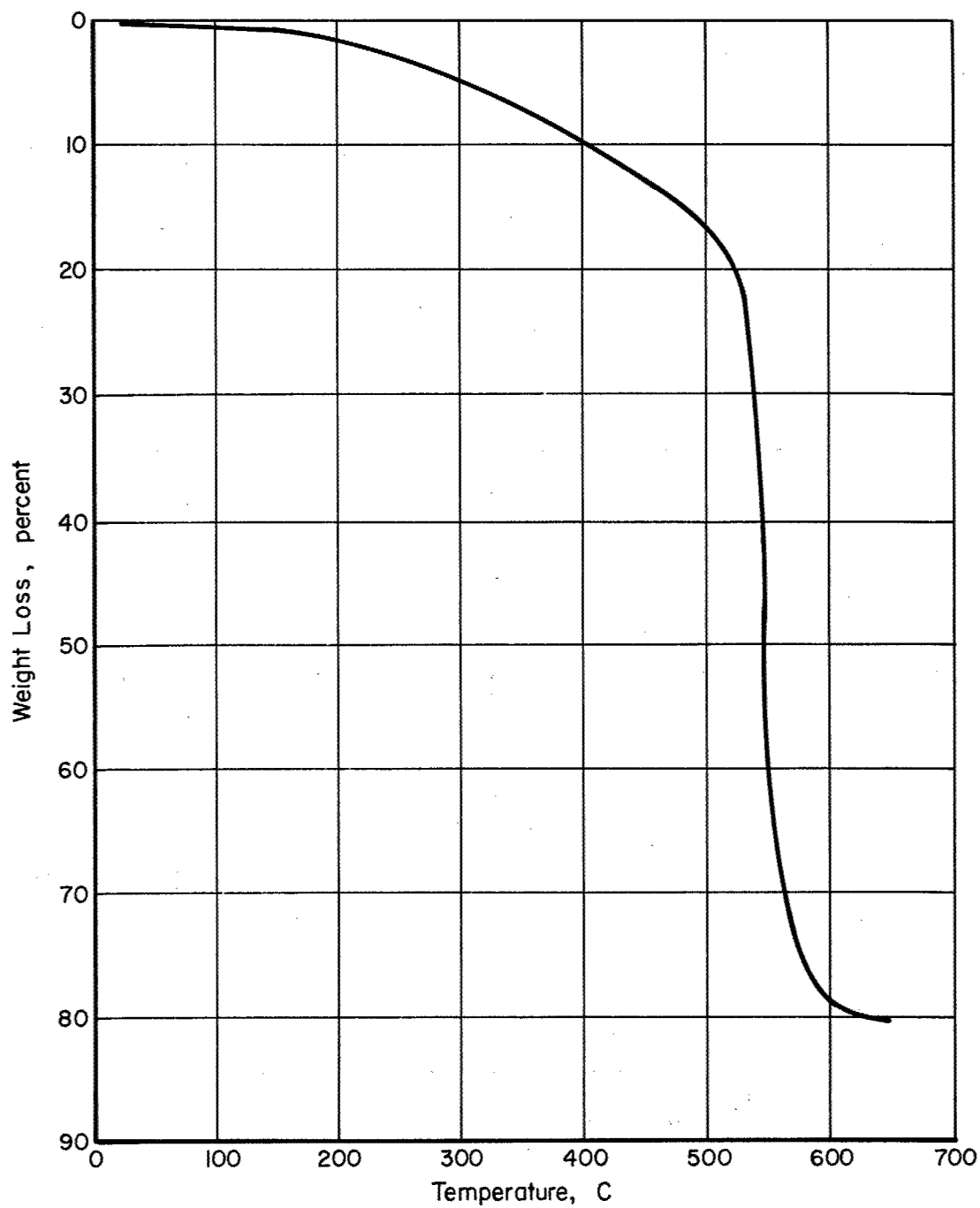


FIGURE 6. TGA THERMOGRAM OF FREEZE-DRIED SILICON-NITROGEN POLYMER SAMPLE HR-109 AT 4C/MIN HEATING RATE AND $\sim 10^{-5}$ TORR USING A 7.76 MG SAMPLE

Conditions

Flow rate: 1.0 ml/min
Temperature: 23 C
Concentration: $4.53(10)^{-4}$ g/ml
Injection: 60 sec
Columns: $3.5(10)^5 - 10^5 - 10^4 - 2(10)^3$
Solvent: THF

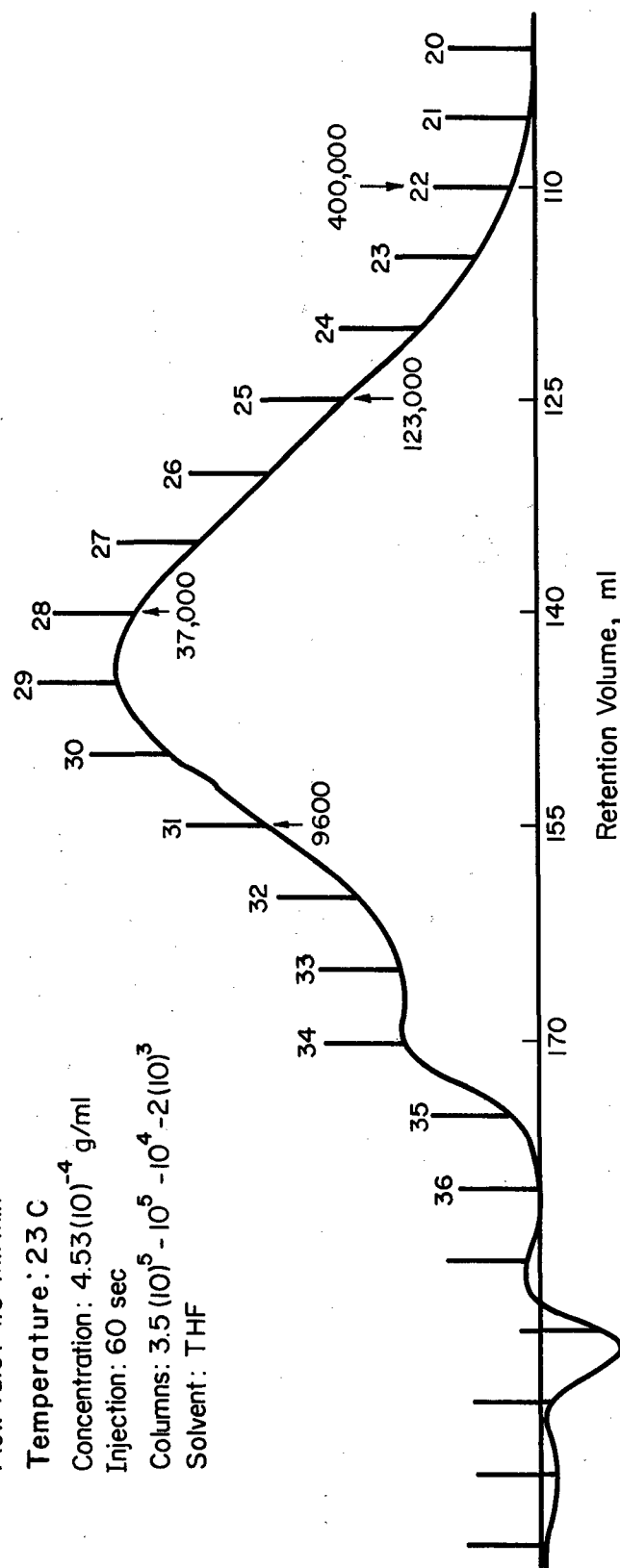


FIGURE 7. GPC CHROMATOGRAM OF SILICON-NITROGEN POLYMER SAMPLE HR-109

Polystyrene molecular weight associated with retention volume indicated at arrows.

Conditions

Flow rate: 1.0 ml/min

Temperature: 23 C

Concentration: $4.345(10)^{-3}$ g/ml

Injection: 60 sec

Columns: $3.5(10)^5 - 10^5 - 10^4 - 2(10)^3$

Solvent: THF

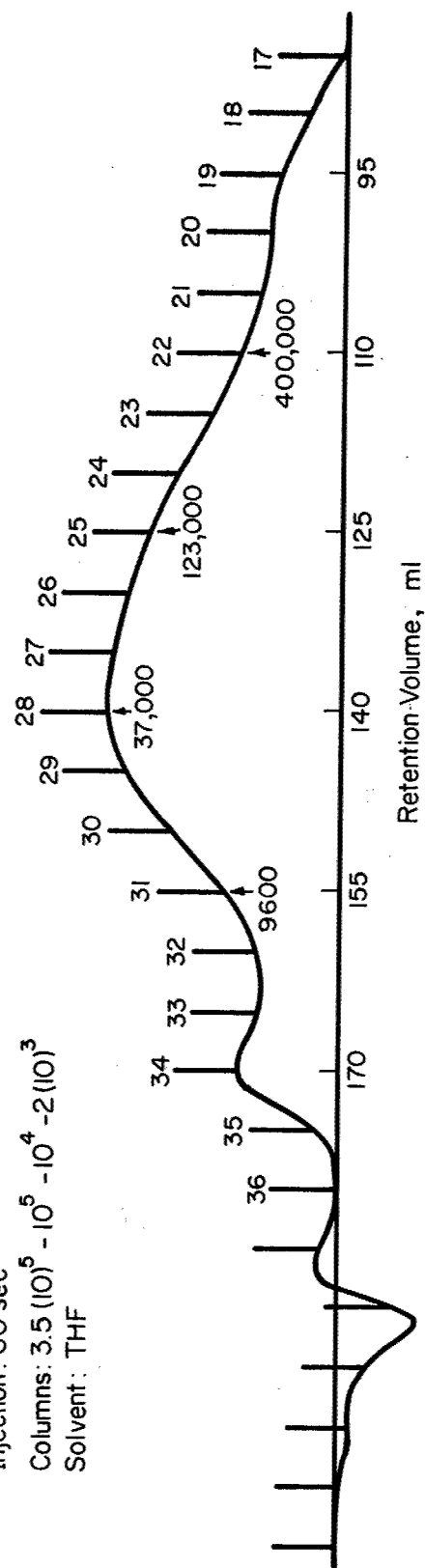


FIGURE 8. GPC CHROMATOGRAM OF SILICON-NITROGEN POLYMER SAMPLE
HR-109 (FREEZE-DRIED)

Polystyrene molecular weight associated with retention volume indicated by arrows.

Conditions

Flow rate: 1.0 ml/min

Temperature: 23 C

Concentration: $4.385(10)^{-3}$ g/ml

Injection: 60 sec

Columns: $3.5(10)^5 - 10^5 - 10^4 - 2(10)^3$

Solvent: THF

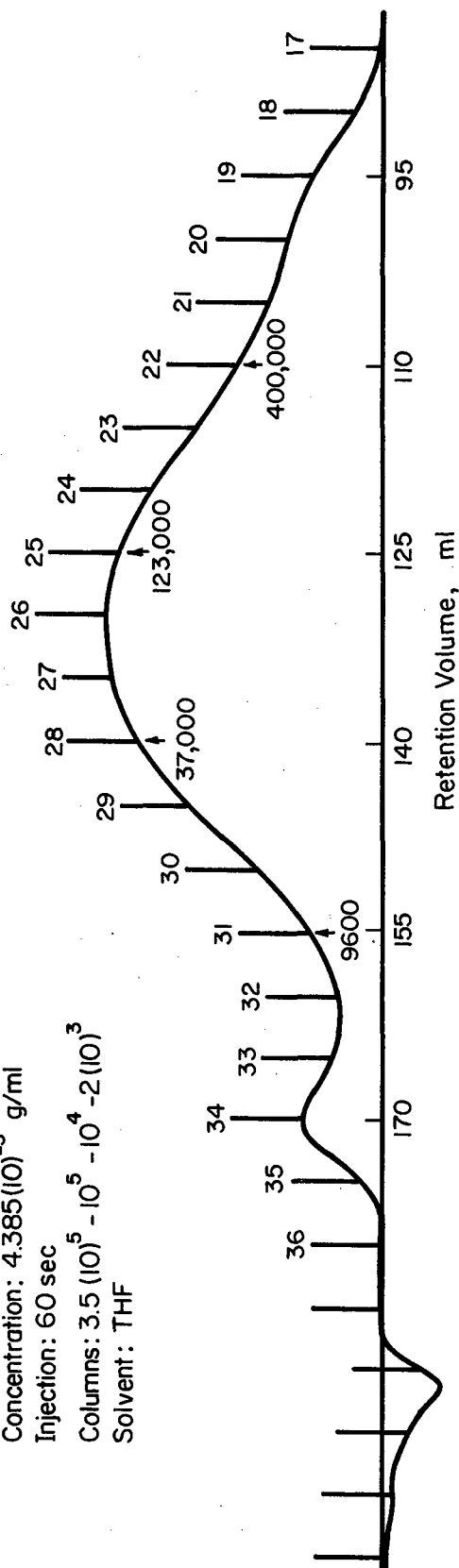


FIGURE 9. GPC CHROMATOGRAM OF SILICON-NITROGEN POLYMER SAMPLE HR-111

Polystyrene molecular weight associated with retention volume indicated by arrows.

Conditions

Flow rate: 1.0 ml/min

Temperature: 23 C

Concentration: $4.41 (10)^{-3}$ g/ml

Injection: 60 sec

Columns: $3.5 (10)^5 - 10^5 - 10^4 - 2 (10)^3$

Solvent: THF

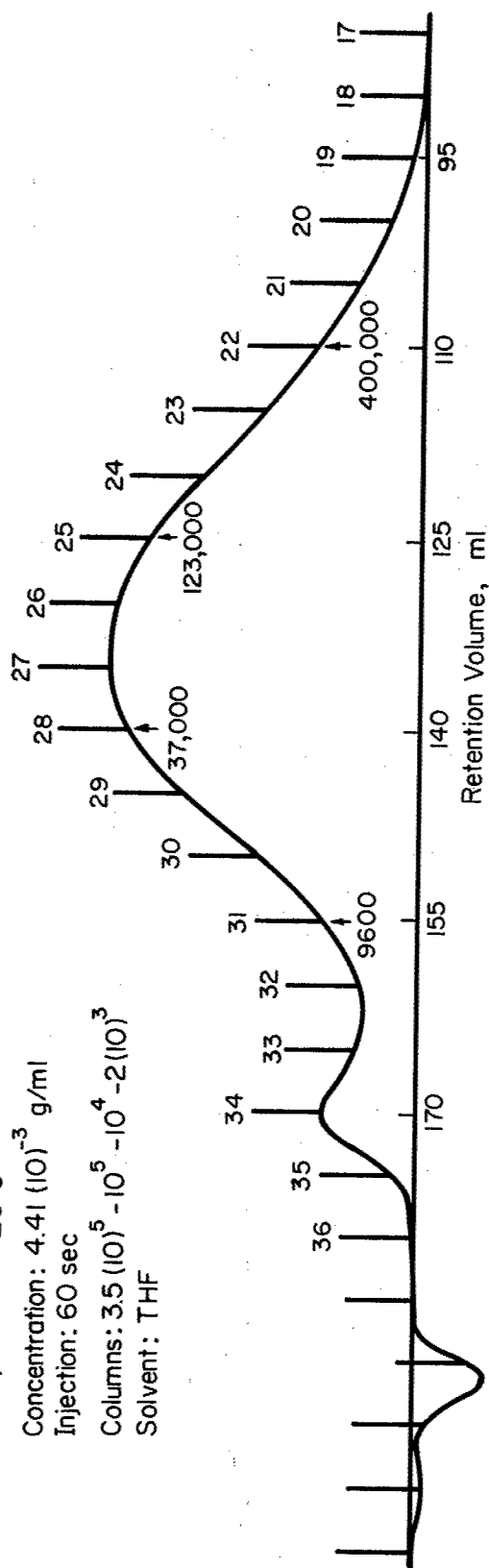


FIGURE 10. GPC CHROMATOGRAM OF SILICON-NITROGEN POLYMER SAMPLE HR-112

Polystyrene molecular weight associated with retention volume indicated by arrows.

retention volume of about 170 ml. This shoulder could arise from unreacted monomer or end-capping agent. However, the polystyrene standard calibration curve suggests that the molecular weight of the species producing the shoulder is in the 800 to 1000 range. A dimeric or trimeric species might be the source.

TABLE II. SOLUTION-VISCOSITY DATA ON SILICON-NITROGEN POLYMERS

Sample	$[\eta]$, dl/g	$\eta_{inh}(a)$, dl/g
HR-109	--	0.28
Freeze-dried HR-109	0.53	--
HR-111	0.69	0.62
HR-112	0.48	0.43

(a) Obtained on 0.5 percent solutions in toluene by MRI.

Since it is planned to use the GPC data to identify synthesis conditions which optimize molecular weight and molecular-weight distribution of this polymer structure, it is desirable to convert the GPC data to a form in which it is independent of the system used to determine it. This is best accomplished by converting the GPC distribution to a molecular weight distribution. Such a conversion requires establishment of a relationship between retention volume and molecular weight, i. e., a calibration curve. As a first approximation to such a relationship, polystyrene "standards" characterized by ArRo Laboratories, Incorporated, were used to provide an indication of the molecular size associated with retention volume. While the hydrodynamic volume could be used to convert the calibration curve obtained with the polystyrene standards to one appropriate for narrow molecular-weight distribution (MWD) silicon-nitrogen polymers⁽⁶⁾, application of such a curve to a broad MWD sample requires correction for zone broadening and skewing⁽⁷⁾. In view of the difficulties associated with these corrections, a relatively new approach for converting GPC data to MWD by use of M_w and M_n data obtained by light scattering and osmometry, respectively, was chosen. In this approach, an artificial calibration curve is constructed which leads to a MWD whose M_w and M_n are equal to that expected from the light scattering and osmometric data. Since the artificial curve embodies corrections for zone broadening and skewing, it will differ from the calibration curve obtained using narrow MWD standards.

The M_w of Sample HR-112 was determined by light scattering from cyclohexane solutions at 30 C. The dn/dc of this polymer in cyclohexane was 0.087 ml/g. The Zimm plot constructed from the light-scattering data, shown in Figure 11, indicates an M_w of 250,000. Comparison of this molecular weight with the observed intrinsic viscosity suggests that the molecule is very compact in toluene, i. e., toluene is not a thermodynamically good solvent.

The number-average molecular weight of Samples HR-112 and HR-109 is being determined by vapor pressure osmometry. Initial results indicate their molecular weights are 7,000 and 11,000, respectively. However, the relative magnitude of these values are inconsistent with the relative M_n predicted from the GPC traces. Therefore, additional effort will be required to establish the source of the inconsistency before the synthetic calibration curve can be constructed.

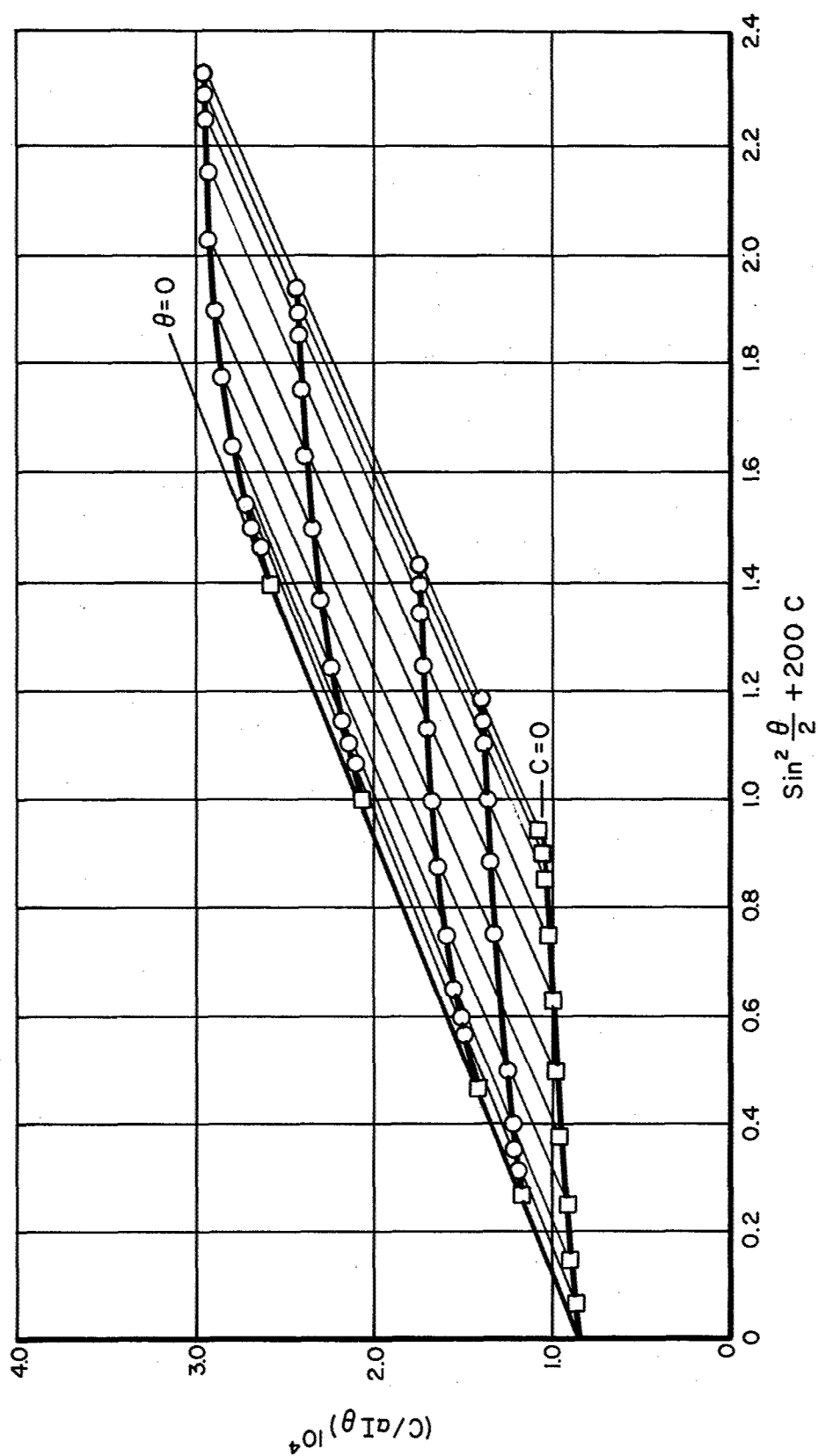


FIGURE 11. ZIMM PLOT FOR SILICON-NITROGEN POLYMER SAMPLE
HR-112 IN CYCLOHEXANE

L. W. Breed et al⁽³⁾ has isolated a polymeric product from the thermally-induced reaction of N,N'-bis (dimethylaminodimethylsilyl) tetramethylcyclodisilazane and *p*-phenylene-bis-(dimethylsilanol). If the reaction has proceeded as expected, characterization of this product should provide data which indicate the effect on properties of substitution of a *p*-phenylene link for the diphenyl ether link contained in the previously characterized samples. A sample of this product, labelled 1074-65, was submitted to Battelle for characterization.

As with the previously characterized Si-N samples, the sample had a strong amine odor when received. The inability to remove the amine odor suggests a continuing reaction with liberation of an amine. The change in solubility from the 38 percent reported by Breed⁽⁸⁾, to less than 5 percent found at Battelle suggests crosslinking is the primary reaction leading to liberation of amine. Breed⁽⁵⁾ has suggested a mechanism for this reaction.

With the exception of silicon, the elemental analyses for this sample, shown in Table III are in good agreement with the proposed structure. The discrepancy between the silicon results obtained by Clark Microanalytical Laboratory and those reported by Breed suggests analytical difficulties. As a check of Clark's technique, the sample was submitted to Spang Microanalytical Laboratory for silicon analysis. The Spang result confirms the existence of difficulty in the silicon analysis. Since Breed used Spang for his analysis, the agreement with the more recent Spang result is surprisingly poor.

TABLE III. ELEMENTAL ANALYSIS OF *p*-PHENYLENE-SUBSTITUTED SILICON-NITROGEN POLYMER 1074-65.

Element	Analysis, percent			
	Calculated	Found(a)	Found(b)	Found(c)
C	44.63	43.68	--	44.03
H	8.26	8.03	--	8.26
N	5.78	6.36	--	5.78
O	6.61	--	--	--
Si	34.71	27.9 ± 1.7(d)	35.89	34.66

(a) Clark Microanalytical Laboratory.

(b) Average of duplicate analyses by Spang Microanalytical Laboratory.

(c) Reported by Breed, et al.⁽¹⁾.

(d) Average of three runs made over a period of 2 days.

A TGA thermogram of the sample (see Figure 12) was obtained between room temperature and 800 C using a 4 C per minute heating rate. Since the weight loss to 200 C was only 1.86 percent, it is unlikely that the DTA endotherm below this temperature was a result of volatilization of impurities. Since the proposed structure of Sample 1074-65 has not been confirmed, a conclusion as to the thermal stability of its structure relative to that of the diphenyl ether linked polymers are subject to question. The thermograms presented in Figures 4 and 12 suggest that substitution of the phenylene link for the diphenyl ether link of HR-109 has substantially reduced the upper service temperature, although a phenylene link is thermally more stable than a diphenyl ether link. This anomaly suggests that the proposed and actual sample structures differ. The difference

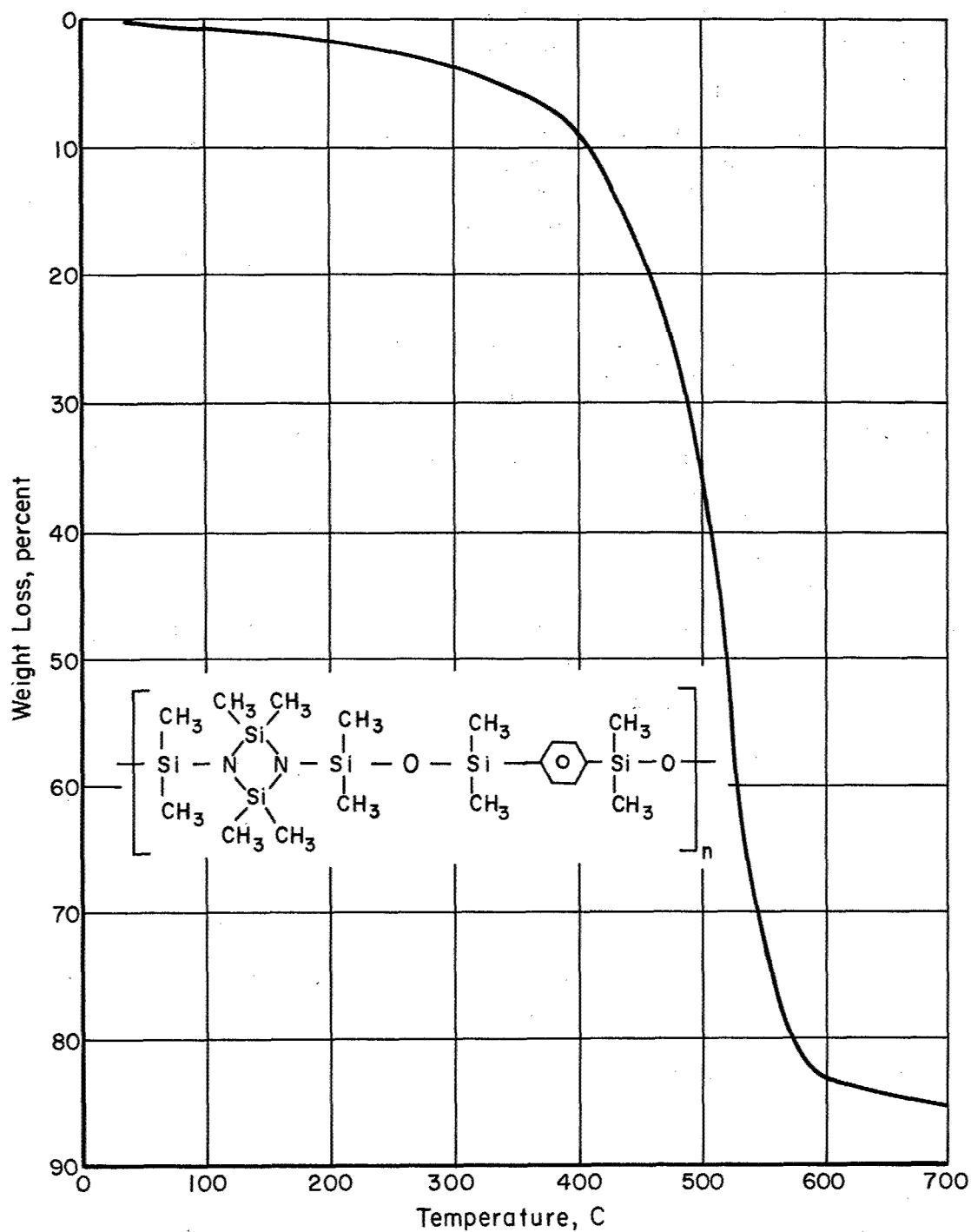


FIGURE 12. TGA THERMOGRAM OF *p*-PHENYLENE-SUBSTITUTED SILICON-NITROGEN POLYMER SAMPLE 1074-65 AT 4C/MIN HEATING RATE AND 0.1 TORR USING A 15.60 MG SAMPLE

in the weight of the residue at 800 C could indicate differences in the mode of fragmentation of these structures. Exposure of the residue to oxygen at 800 C did not appreciably change its weight, suggesting that it was SiO₂.

A thorough solvent search with 1074-65 using the microscopic technique⁽¹⁾ did not indicate complete solubility in any solvent. However, substantial and rapid polymer swelling occurred in alkanes, ethers, ketones, simple aromatics, and their fluorinated analogs. If this sample is crosslinked, a noncrosslinked sample would probably be soluble in most or all of these solvents. Slight swelling was observed in nitroalkanes and nitriles, while no reaction was noted for alcohols, amides, or sulfoxides. The solvents tested, as well as their pertinent thermodynamic properties, are listed in Table IV. The solvent formulating map generated with this sample is shown in Figure 13.

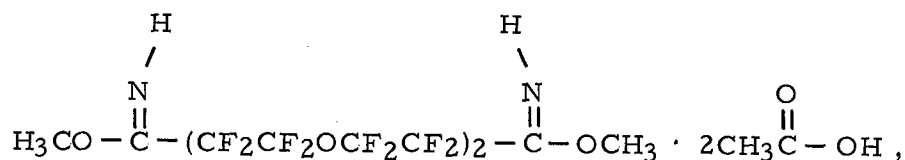
The volume change on swelling in toluene at 23 C for silicon-nitrogen polymer 1074-65 was determined with a Jolly Balance (for a description see reference 2). The 430 percent volume increase (average of two runs) indicates a moderate crosslink frequency comparable with the previously characterized Si-N samples⁽²⁾.

The sample was examined by DTA between room temperature and 700 C using a heating rate of 4 C per minute. The thermogram is shown in Figure 14. The broad endotherm between 50 and 200 C may be a result of continuation of crosslinking and liberation of dimethylamine. The very broad exotherm above 200 C probably reflects sample pyrolysis. Start of the exotherm at 200 C suggests that pyrolytic breakdown begins at this temperature.

The sample was also examined by Tracor, Incorporated (Austin, Texas) on their H-5 subambient DTA. The slope change in the thermogram at about -38 C (see Figure 15) is interpreted as the glass-transition temperature of this sample. This transition is somewhat lower than for the previous Si-N samples, although the *p*-phenylene link would be expected to reduce chain flexibility and thereby raise the glass transition temperature. The inconsistency is probably a result of differences between the proposed and actual sample structures.

Perfluoroalkyl Bibenzoxazole Polymers

Two polymer samples prepared at Dow Chemical Company were received. These samples, labelled 9659-129 and 9659-140, were prepared by the reaction of dihydroxybenzidine with



in the case of Sample 9659-140, and with

TABLE IV. SOLVENTS USED IN SOLVENT SEARCH WITH p-PHENYLENE-SUBSTITUTED SILICON-NITROGEN POLYMER 1074-65 AND PERTINENT THERMODYNAMIC PROPERTIES

Solvent	Literature Boiling Point, C	Solubility Parameter, $\delta \left(\frac{\text{cal}}{\text{cc}} \right)^{1/2}$	H-Bonding Index, $\gamma^{(a)}$	Dipole Moment, $\mu^{(a)}$
Decane	174	6.6	0	0
n-Hexane	69	7.3	0	0
Cyclohexane	81	8.2	0	0
Toluene	110	9.2	4.5	0.4
Benzene	80	9.2	0	0
Carbendisulfide	46	10.0	0	0
Nitrobenzene	211	10.0	2.8	4.3
Acrylonitrile	78-9	10.5	5.7	3.8
Nitroethane	115	11.1	2.5	3.6
Acetonitrile	82	11.9	6.3	3.9
Nitromethane	101	12.7	2.5	3.4
Ethylenecarbonate	255	14.7	4.9	1.0
Malononitrile	220	15.1	2.5 ^(b)	
Dibutylether	142	7.1	11.0	1.2
Diethylether	35	7.4	13.0	1.2
Diisopropylether	68	7.8	12.3	1.2
2-Undecanone	228	7.8	7.9	2.7
Methylethylketone	80	9.3	7.7	2.7
1,4-Dioxane	101	9.9	9.7	0
Acetone	56	10.0	9.7	2.9
N,N-diethylformamide	177-8	10.6	11.7	2.0
N,N-dimethylacetamide	165	10.8	12.3	2.0
N,N-dimethylformamide	153	12.1	11.7	2.0
N-Ethylacetamide	205	12.3	12.0	2.0
Dimethylsulfoxide	189	12.9	7.7	4.0
N-Ethylformamide	198	13.9	12.0	2.0
Dimethylsulfone	241	14.5		4.5
γ -Butyrolactone	206	15.5	9.7	2.7
N-Methylformamide	198	16.1	12.0	2.0
Diethylamine	56	8.0	18.0 ^(b)	0.9
Hexamethylphosphoramide	170	10.5	18.0 ^(b)	--
Pyridine	116	10.7	18.1	2.2
2-Propanol	82	11.0	18.7	1.6
Aniline	184	11.8	18.1	1.5
N,N-Dimethylaniline	193	12.0	14.3	1.5
Formic Acid	100	12.1	18.0 ^(b)	1.5
Ethanol	78	12.7	18.7	1.7
Methanol	65	14.5	18.7	1.7
Formamide	195	19.2	18.0	3.2
Methanesulfonic Acid				
Hexafluoroxylene	116	7.5	--	0
Benzotrifluoride	101-2	8.1	--	--
Hexafluorobenzene	81-2	8.2	--	--
m-Bromobenzotrifluoride	153.4	8.6	--	--

(a) From Crowley(9).

(b) Estimated Value.

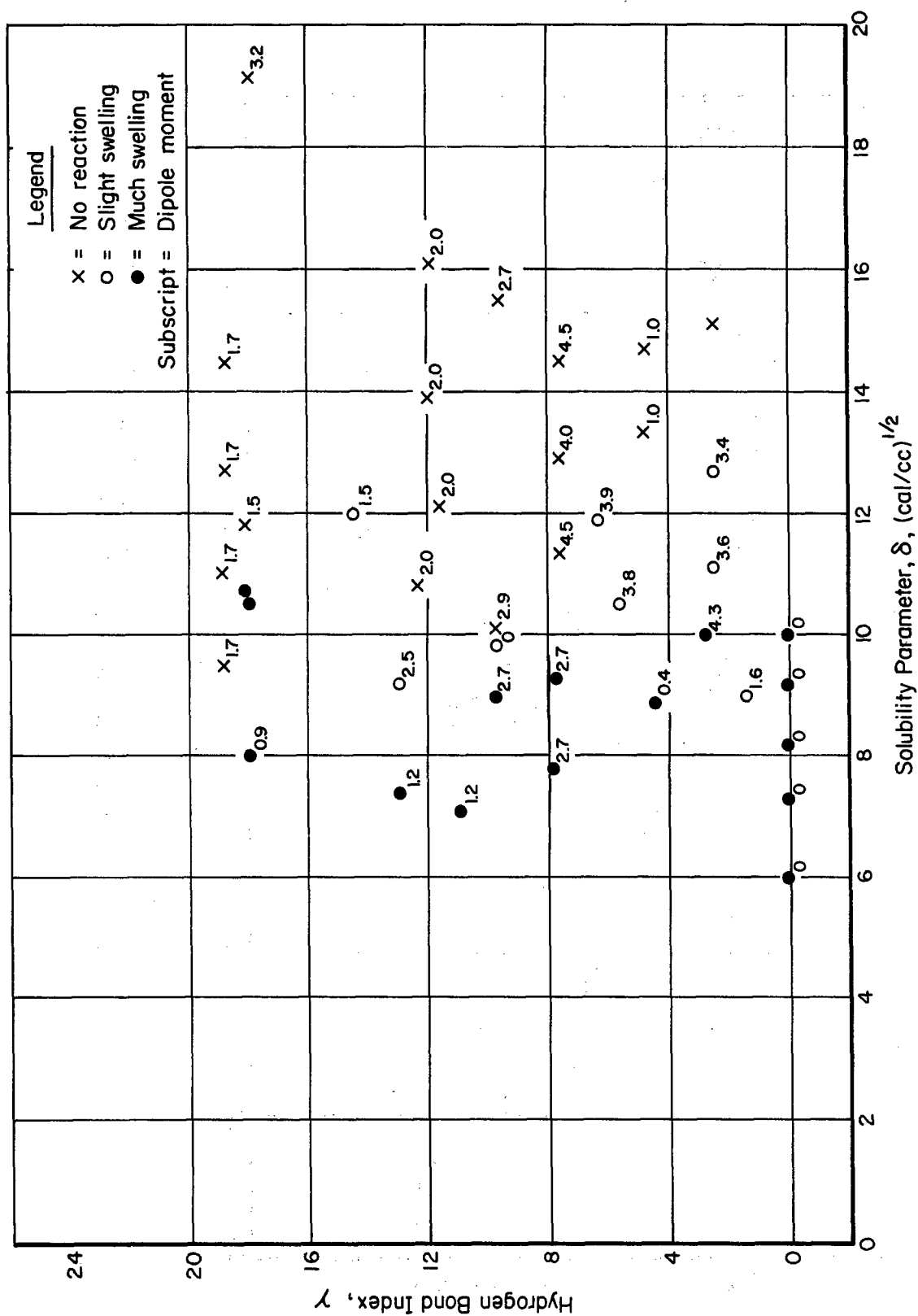


FIGURE 13. SOLVENT FORMULATING MAP FOR p-PHENYLENE-SUBSTITUTED SILICON-NITROGEN POLYMER SAMPLE 1074-65

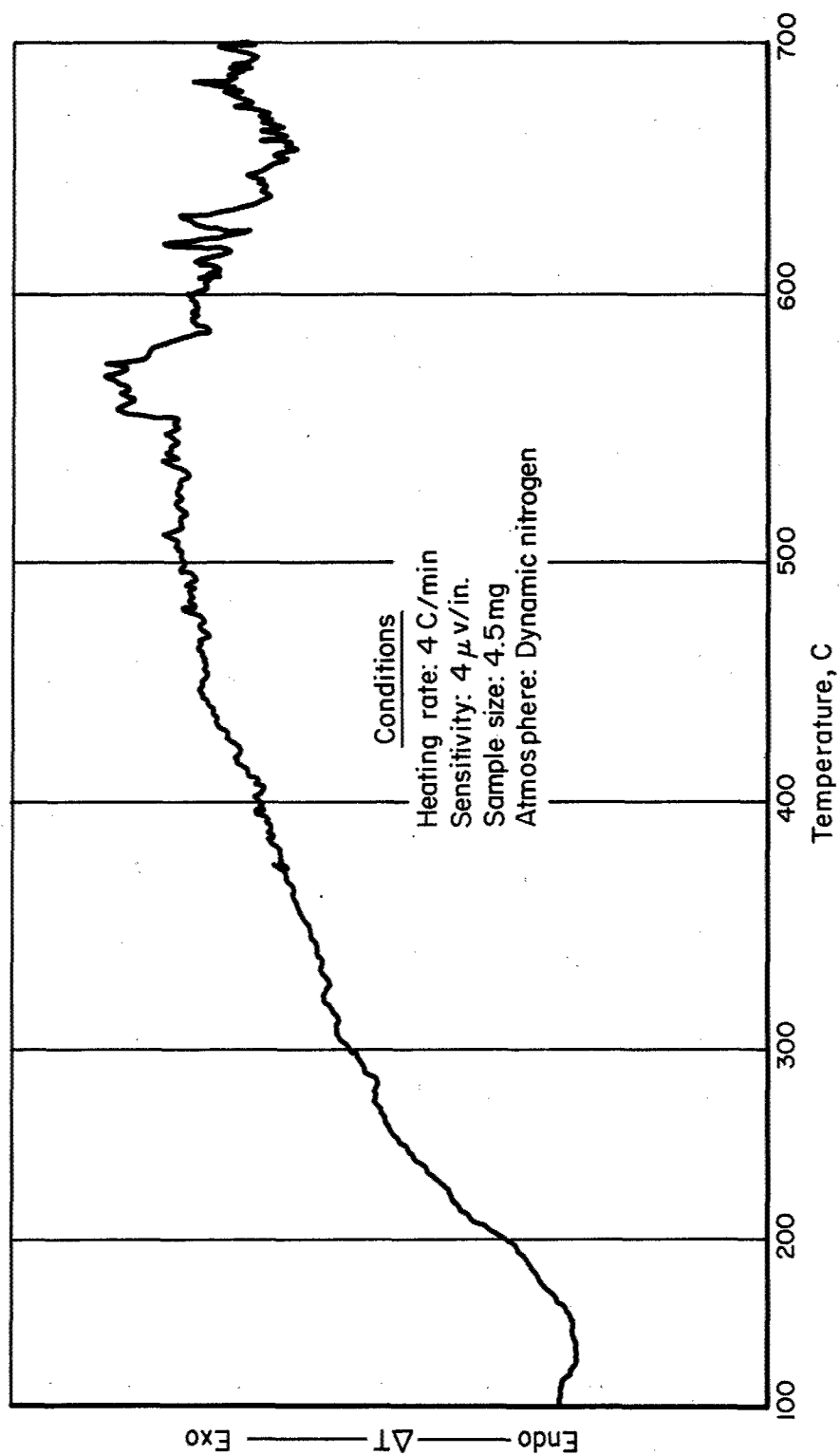


FIGURE 14. DTA THERMOGRAM OF p-PHENYLENE-SUBSTITUTED SILICON-NITROGEN POLYMER SAMPLE 1074-65

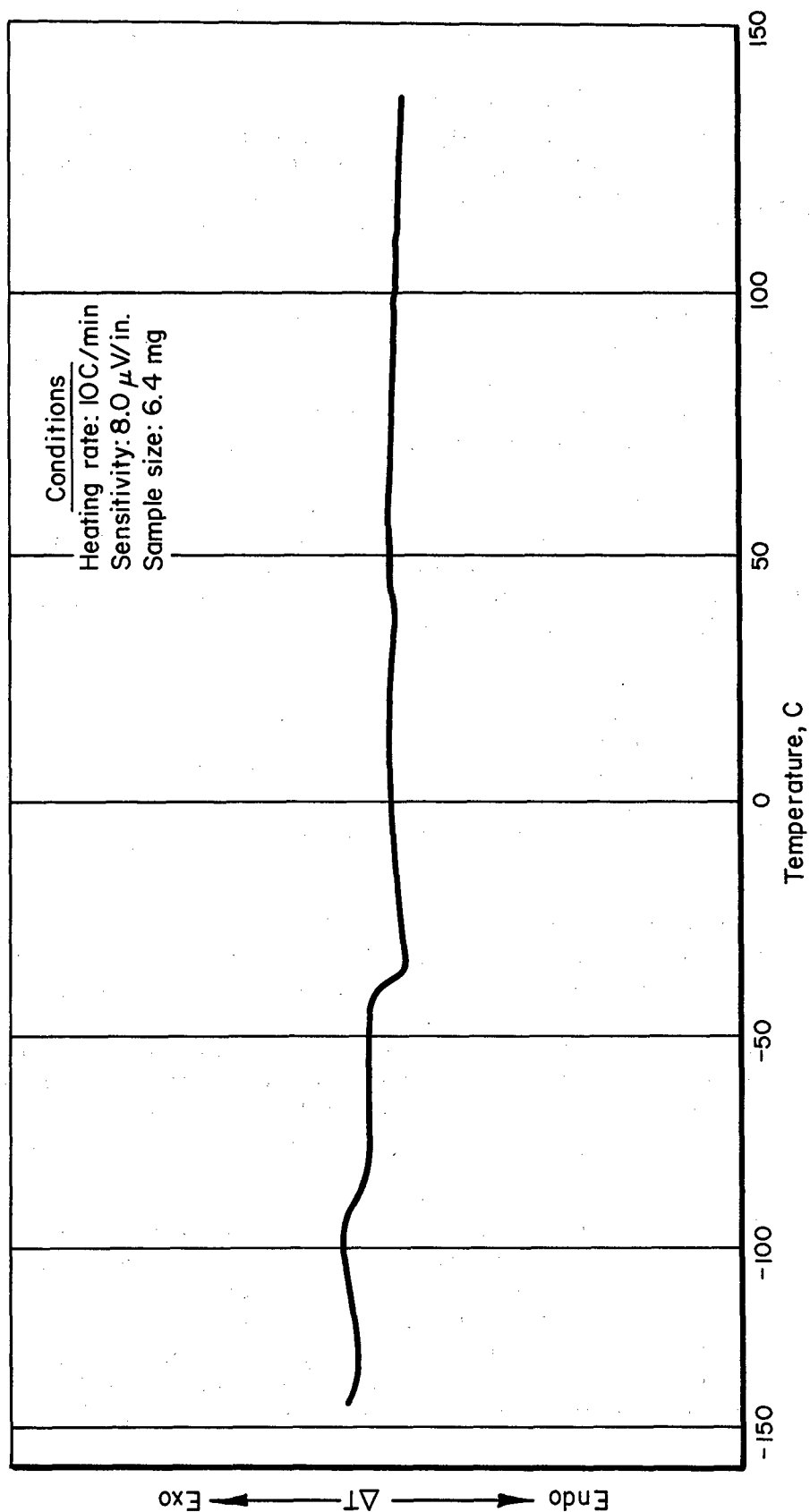
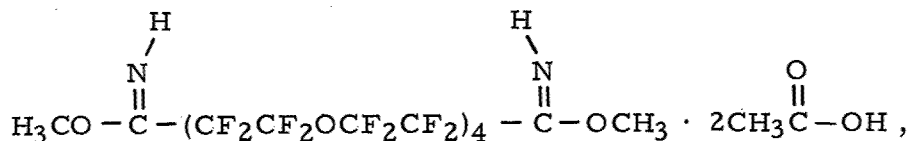


FIGURE 15. SUBAMBIENT DTA THERMOGRAM OF p-PHENYLENE-SUBSTITUTED SILICON-NITROGEN POLYMER SAMPLE 1074-65



to produce Sample 9659-129. The longer link between the bibenzoxazole groups in these samples than was present in the previously characterized nonelastomeric samples (perfluorosebacate bibenzoxazole) is expected to introduce more chain flexibility and thereby produce elastomeric properties. The hard gum-like properties of the as-received samples suggests that the structure modification has produced the expected result to some degree.

The differences in the TGA thermograms of these samples (see Figure 16) casts doubt on the structure of one of them. Since structural defects would be expected to reduce thermal stability, it appears likely that Sample 9659-129 has appreciable defects. If this is the case, then samples of the idealized structure indicated for Sample 9659-140 could have upper service temperatures below 450 C.

Subambient DTA thermograms were obtained on Sample 9656-129. One of these, shown in Figure 17, indicates a broad transition at approximately -10 C and an additional transition at 12 C. These transitions were confirmed by thermograms obtained with different amounts of sample. The longer straight-chain link between bibenzoxazole rings in Sample 9659-140 suggests that lower transition temperatures can be expected.

The inherent viscosities of the samples were measured in hexafluoroisopropanol at 30 C. These were 0.23 dl/g and 0.28 dl/g for Sample 9659-140, and Sample 9659-129, respectively. In addition, the intrinsic viscosity of Sample 9659-140 was measured in trifluorotoluene (TFT) at 30 C. The 0.17 dl/g observed indicates TFT is a poorer solvent than hexafluoroisopropanol. The observed Huggins' constants indicated no appreciable association in this solvent.

A solvent search was performed with Sample 9659-140 by the microscopic technique⁽¹⁾ using the list of solvents in Table XI. None of the solvents included in the list dissolved the sample. However, greater than 0.1 percent solutions were obtained in hexafluoroisopropanol, benzotrifluoride, hexafluoroxylene, and hexamethylphosphoramide. At present, we have not been able to devise an effective means for estimating the divided solubility parameters of these solvents which would permit inclusion of them in the standard list. The solvent formulating map (Figure 18) suggests that this material reacts with many common solvents as was the case for the silicon-nitrogen polymers.

The molecular weight of the previously characterized⁽²⁾ sebacate polymers (Samples 9659-94H and 10295-78H) and the new elastomeric polymers (Samples 9659-129 and 9659-140) are of interest; the former, to indicate the success of the synthesis chemistry involved, and the latter as an indication of the significance of the measured thermal properties. Previously reported inherent viscosity - molecular weight data for the sebacate polymers⁽¹⁰⁾ appear to be inconsistent. A possible source of the inconsistency is the use of membrane osmometry to measure number-average molecular weights

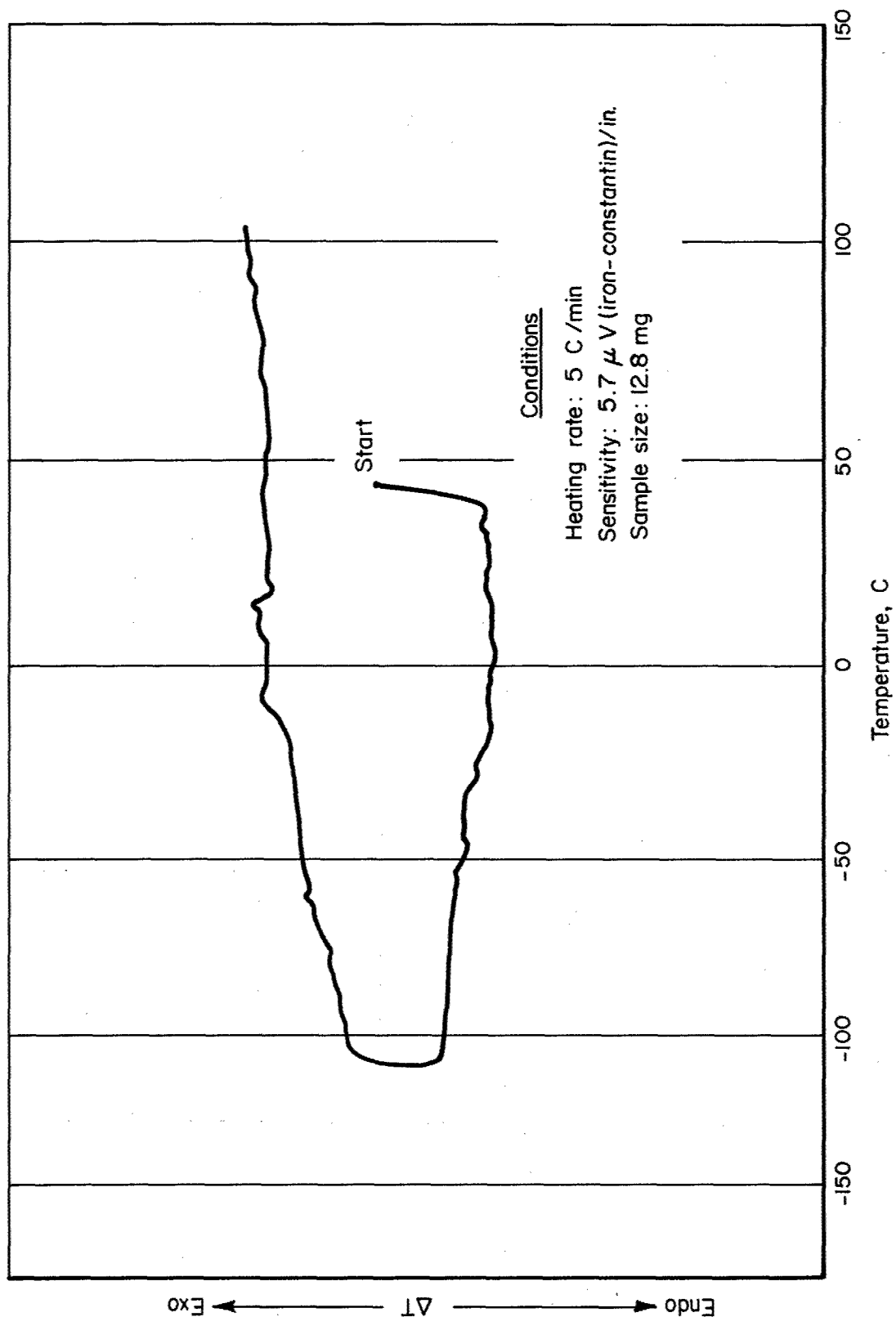


FIGURE 17. SUBAMBIENT DTA THERMOGRAM OF POLY(PERFLUOROALKYLETHER BIBENZOXAZOLE) POLYMER SAMPLE 9659-129

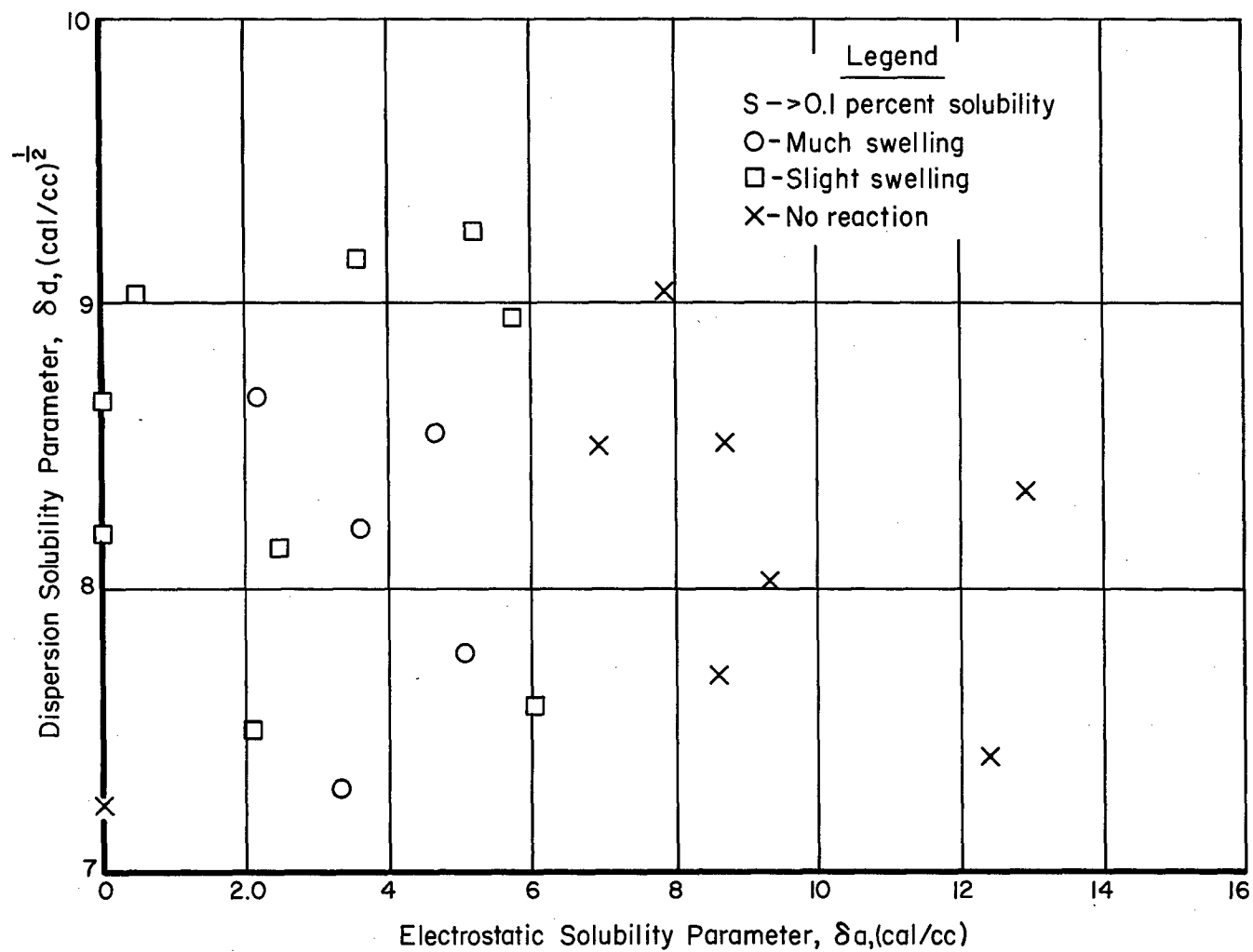


FIGURE 18. SOLVENT FORMULATING MAP FOR POLY-(PERFLUOROALKYLETHER BIBENZOXAZOLE) SAMPLE 9659-140

that apparently are below 20,000. Initial efforts at Battelle to determine molecular weights of these samples were by use of vapor-pressure osmometry. However, the low heat of vaporization and the strong affinity for water of hexafluoroisopropanol (HFI), the only feasible solvent, prevented analysis by vapor-pressure osmometry.

Since the osmometric techniques for molecular-weight measurement could not be used with these polymers, the more expensive light-scattering technique was investigated. The only solvent for the sebacate polymers is HFI. Hence, its appropriateness for light scattering was investigated. The dn/dc of solutions of the polymers were all adequate for light scattering, i. e., greater than 0.01. The dn/dc values for Samples 9659-94H and 10295-78H are 0.153 and 0.151, respectively. Within experimental error, the values are the same, suggesting that the structures of the samples are very similar.

During initial work with HFI, several undesirable effects on personnel were observed. Headache, eye irritation, numbing of extremities, leg cramps, and hyperemia were all attributed to exposure to HFI. As a result of these effects, subsequent handling was only permitted in polyethylene "glove bags" which were purchased from Instruments for Research and Industry (Cheltenham, Pa.). In addition to reducing personnel exposure, use of the glove bags is expected to greatly reduce the chances for moisture pickup by the solvent. Therefore, solvent scattering-intensity changes from moisture pickup will be minimized.

Severe difficulty was encountered in clarification of HFI for light scattering. Initially, the apparatus shown on the left of Figure 19 was assembled to permit repeated filtrations without exposure to the air. The "T" valves are rotated so that the solvent passes through the filter but returns through the Teflon tubing. However, even 12 passes through a 0.5- μ Millipore Solvinox filter failed to remove particles sufficiently large to cause gross instability of scattering-intensity readings. The difficulty was attributed to inability to remove particulate matter from the light-scattering cell by washing with HFI. The "modified" apparatus in Figure 19 was assembled to avoid the problem. Since filtration required sustained application of pressure on the solvent, the upper syringe was pressurized with N_2 to make performance of the filtration step easier. The cleanliness of the light-scattering cell was checked by measuring the z -value of clarified benzene in the cell. Once a z -value less than 1.01 was obtained, the benzene was discarded and the cell inverted to permit drainage. After 18 passes through the modified filtration apparatus, HFI was transferred to the "clean" light scattering cell. The solvent still contained sufficient particulate matter to make the scattering intensity unstable. The possibility that what was suspected to be particulate matter in the solvent was actually air bubbles was eliminated by allowing the filtered solution to stand in the light scattering cell for 16 hours before attempting to measure its scattering envelope.

Although the sebacate polymers are sufficiently soluble for light scattering analysis only in HFI, several fluorinated solvents have been identified in which sufficiently concentrated solutions of the new elastomers can be prepared. The higher boiling point and lesser tendency for water pickup than HFI indicated trifluorotoluene (TFT) might be a good choice. TFT was successfully clarified and the dn/dc of solutions of Sample 9659-140 was acceptable for light scattering. Initial light-scattering results indicated that the sample had a molecular weight in excess of 100,000. However, a peculiar Zimm plot (concave upward) casts doubt on the validity of these results.

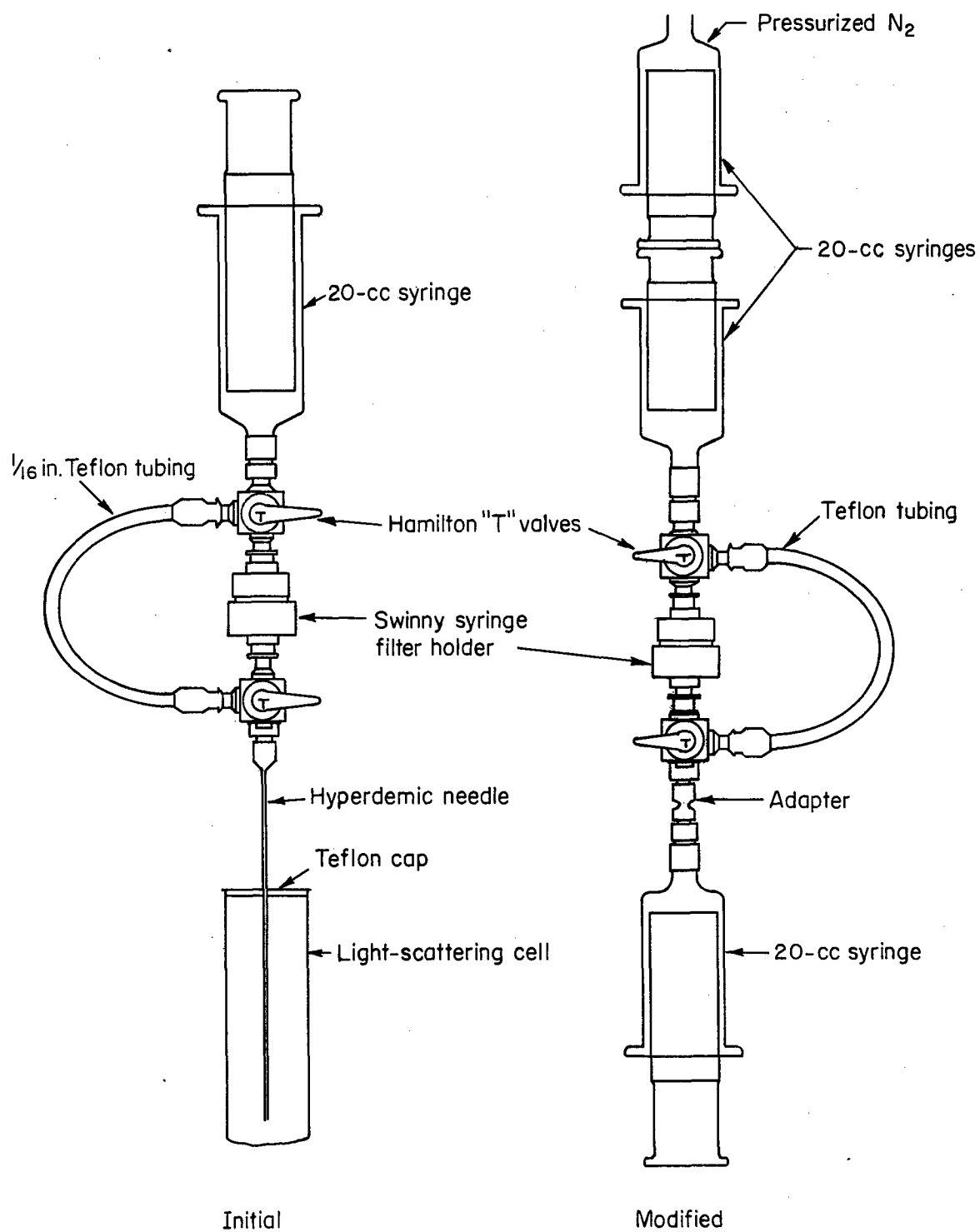


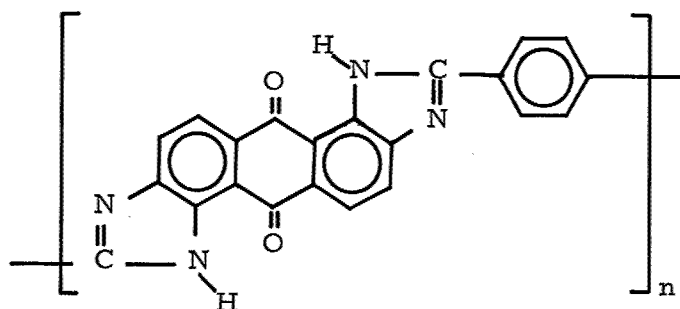
FIGURE 19. APPARATUS FOR CLARIFICATION OF SOLVENTS FOR LIGHT SCATTERING

Measurement of the scattering intensity with a filter in the scattered beam which was opaque to the incident frequency indicated that the sample was fluorescing appreciably. Preliminary measurement with an interference filter in the scattered beam which only passes the incident frequency (50 percent transmittance at $\pm 25\text{\AA}$ from incident frequency) indicated the molecular weight of the sample is considerably below 100,000. This is in line with the molecular weight of a random-coil polymer with an intrinsic viscosity of 0.17 dl/g.

To have sufficient sample to prepare solutions of appropriate concentration for light scattering, it was necessary to recover the polymer from the solutions used in the previous preliminary measurements. The solutions were freeze dried, the residue redissolved in TFT, and precipitated with anhydrous methanol. However, the IR spectrum of the precipitate did not correspond to the spectrum of the initial sample. Therefore, additional material will be required and appropriate solvents identified before light-scattering determination of molecular weight can be performed.

Polypyrrolone Polymers

A sample of polymeric product of the thermally induced condensation of 1,2,5,6-tetraaminoanthraquinone with the dibisulfite adduct of terephthalaldehyde, labelled PE-68, was received for characterization. The sample was prepared in C. S. Marvel's laboratory and is believed to have the structure



Elemental analysis of this sample, shown in Table V is in good agreement with the proposed structure.

TABLE V. ELEMENTAL ANALYSIS OF POLY-PYRROLONE POLYMER SAMPLE PE-68

Element	Analysis, percent	
	Calculated	Found(a)
C	72.93	72.33
H	2.76	3.33
N	15.47	15.19
O	8.84	9.15(b)

(a) Clark Microanalytical Laboratory - average of two runs.

(b) By difference.

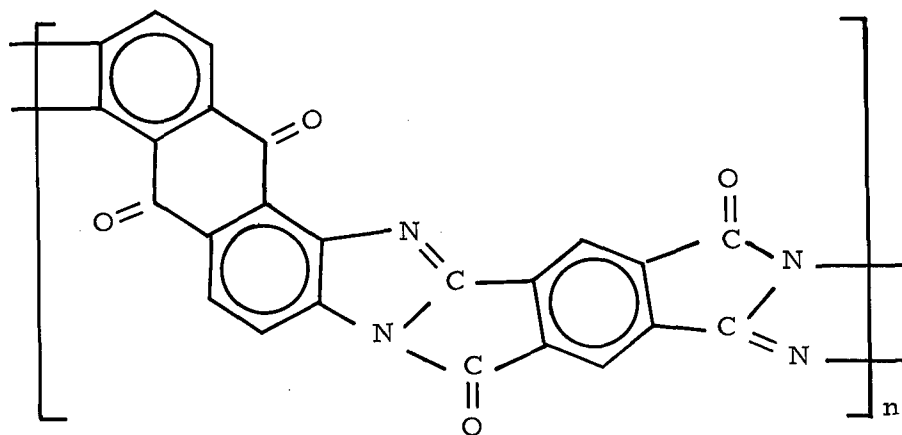
A solvent search with Sample PE-68 using the microscopic technique⁽¹⁾ and the solvents listed in Table V indicated that solutions formed only in highly acidic solvents. A dark red-orange solution was produced with methanesulfonic acid and some interaction with formic acid was observed in addition to formation of solution in sulfuric acid. There was no observed interaction with the other solvents tested.

The IR spectrum of the sample (see Figure 20) contains strong evidence for N-H, C-N, and C=N bonds along with aromatic C-C. A strong band between 1200 and 1300 cm^{-1} could include absorption from anthraquinone, aromatic amine, aromatic acid, and cyclic anhydride.

The DTA thermogram of this sample, Figure 21, provided no evidence for a glass transition or crystalline melting. The endothermal peak at 68 C is probably indicative of solvent loss.

The TGA thermogram (see Figure 22) of this sample suggests that the upper service temperature of materials with this structure is below about 550 C. The initial weight loss of about 4 percent was found by mass spectral analysis of the volatiles to be caused by loss of water. Nitrogen, water, and carbon dioxide were identified in the volatiles of the sample at 400 C.

A sample of a different polypyrrolone polymer prepared in C. S. Marvel's laboratory and labelled PE-82 was received for characterization. The sample was prepared by polycondensation of 1, 2, 5, 6-tetraaminoanthraquinone (TAA) with pyromellitic acid dianhydride (PMDA) and is believed to have the structure



It should be noted that, if the proposed structure is attained, the polymer has no single links, i. e., it is a true ladder polymer, in contrast with PE-68.

The results of elemental analysis shown in Table VI are not in good agreement with those calculated from the proposed structure. If one calculates the elemental content expected if 4 moles of water per repeat unit are present, better agreement with the observed elemental content is obtained. Since the material is polymeric, the water suggested by the elemental analysis is probably indicative of incomplete cyclodehydration and retained water.

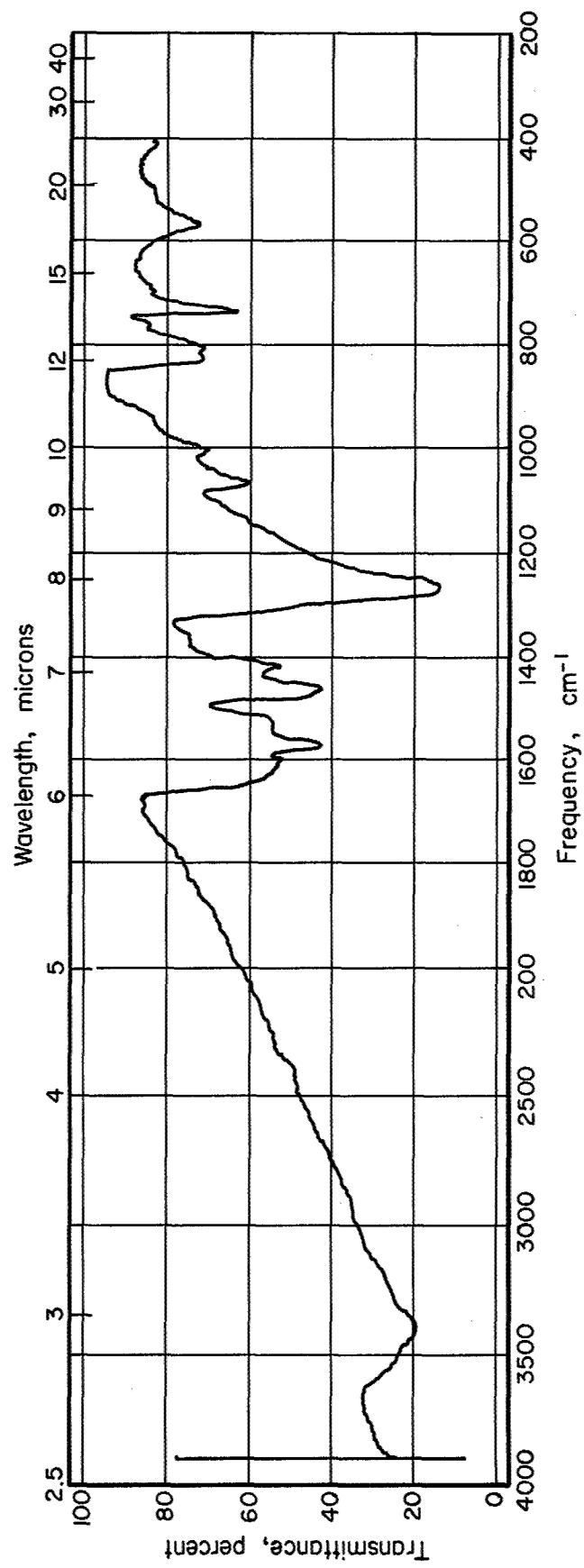


FIGURE 20. INFRARED SPECTRUM OF POLYPYRROLONE POLYMER
SAMPLE PE-68

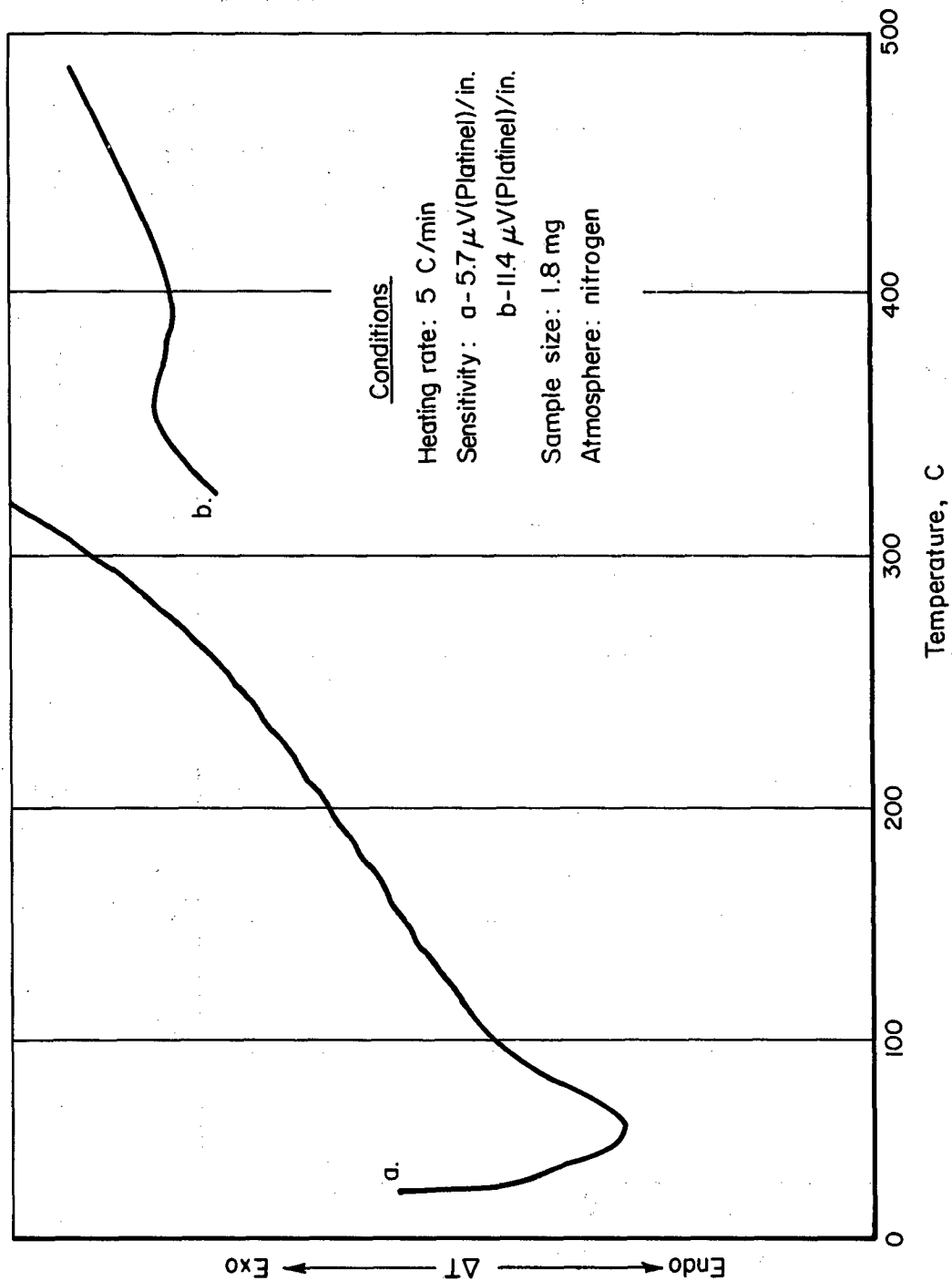


FIGURE 21. DTA THERMOGRAM OF POLYPYRROLONE POLYMER SAMPLE PE-68

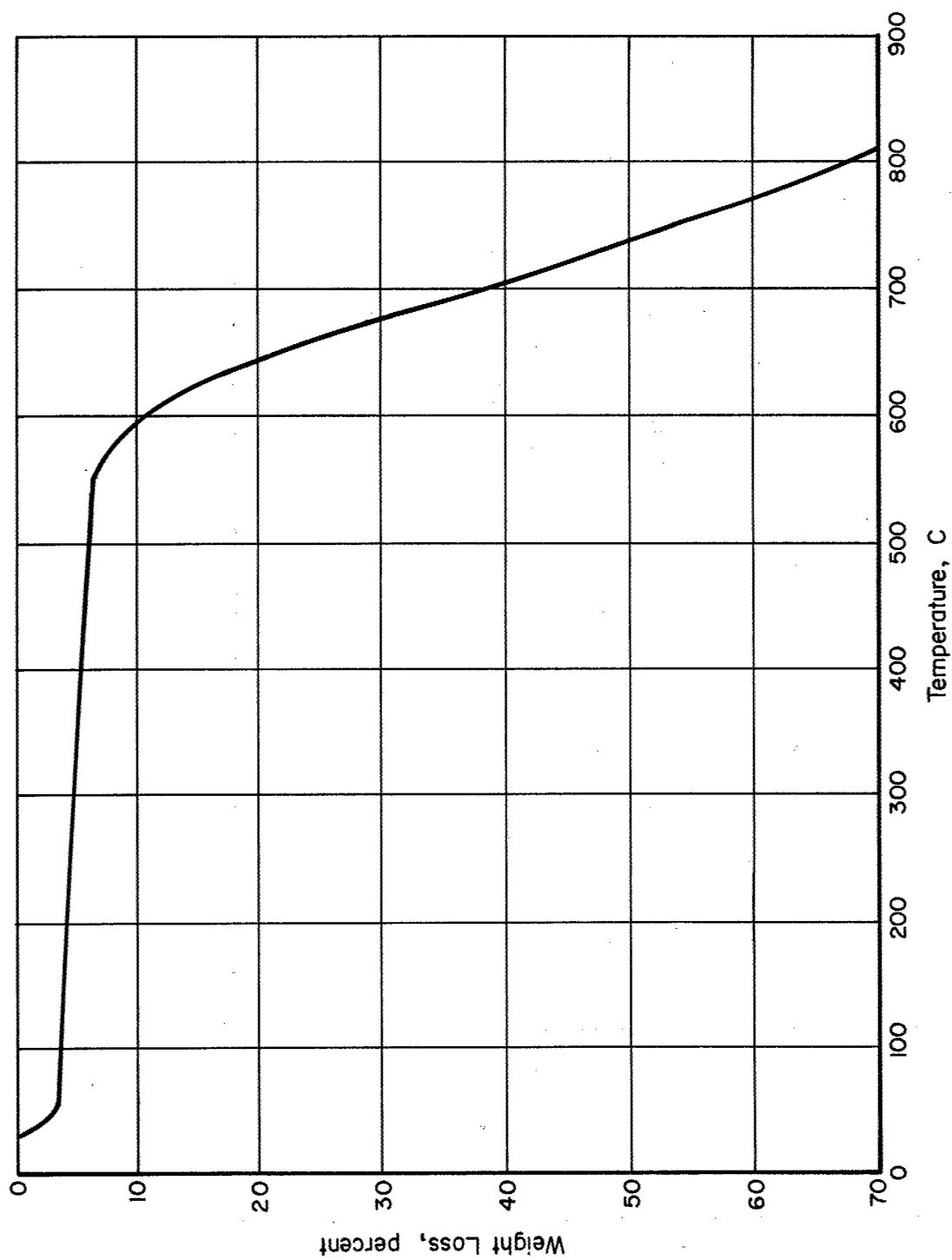


FIGURE 22. TGA THERMOGRAM OF POLYPYRROLONE POLYMER SAMPLE PE-68
AT 4C/MIN HEATING RATE AND 0.1 TORR USING A 4.60 MG SAMPLE

TABLE VI. ELEMENTAL ANALYSIS OF POLYPYRROLONE POLYMER
SAMPLE PE-82

Element	Analysis, percent		
	Calculated for Proposed Structure	Calculated for Proposed Structure + 4 moles H ₂ O	Found(a)
C	69.56	59.26	60.36
H	1.45	2.88	3.67
N	13.53	11.52	11.20
O	15.46	26.34	24.76(b)

(a) Average of duplicate analysis.

(b) By difference.

The IR spectrum (see Figure 23) contains evidence for an aromatic carboxylic acid in agreement with the incomplete cyclodehydration suggested by the elemental analysis. As in Sample PE-68, there is a strong band between 1200 and 1300 cm⁻¹, indicative of absorption from anthraquinone, aromatic amine, aromatic acid, and cyclic anhydride.

A solvent search using the microscopic technique⁽¹⁾ and the solvents listed in Table VII, indicated solubility in highly acidic solvents. This is expected for a sample with basic nitrogens. A dark-green solution was obtained with this sample in methanesulfonic acid in contrast with the dark red-orange solution obtained with Sample PE-68. When this sample was left in contact with several solvents for 4 to 6 hours, discoloration of the solvents was observed. Sample PE-68 was also examined in the solvents where PE-82 reacted slowly. The solvents where the reactions occurred are listed in Table VII. A solvent formulating map for PE-82 is shown in Figure 24.

TABLE VII. INTERACTIONS OF POLYPYRROLONE POLYMER
SAMPLES PE-82 AND PE-68 WITH VARIOUS
SOLVENTS

Solvent	Color Change(a)	
	PE-82	PE-68
Formic acid	Pale yellow	Dark red
Dimethylacetamide	Dark yellow	Orange-brown
Dimethylformamide	Orange-brown	Orange-brown
Diethylformamide	Dark yellow	Yellow-brown
N-Ethylacetamide	Pale yellow	None
N-Ethylformamide	Yellow	None
N-Methylformamide	Reddish-black	None
Formamide	Yellow	None
Dimethylsulfoxide	Orange	Red-brown

(a) Solvents are initially water-white liquids.

The DTA thermogram of Sample PE-82, Figure 25, suggests loss of surface volatiles between room temperature and 100 C followed by a gradual exothermal process between 100 and 500 C. The shape of the thermogram above 100 C suggests that the

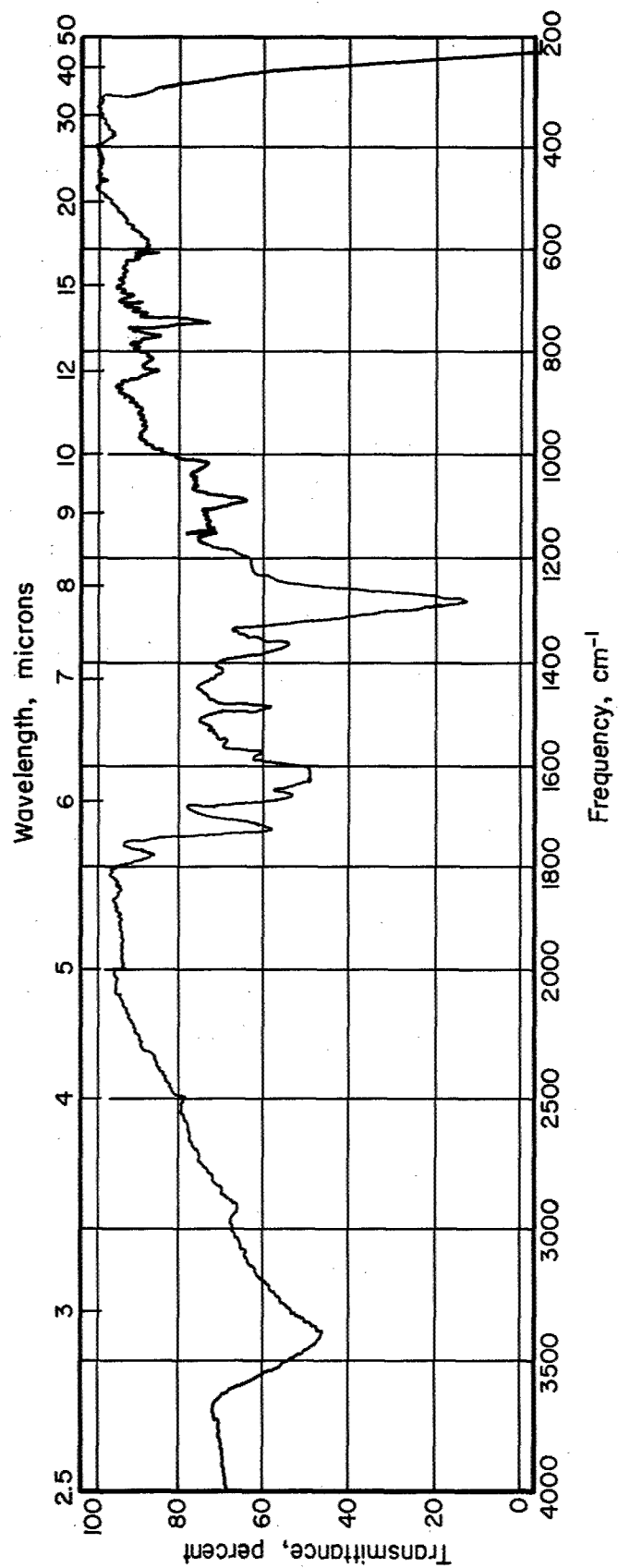


FIGURE 23. INFRARED SPECTRUM OF POLYPYRROLONE POLYMER
SAMPLE PE-82

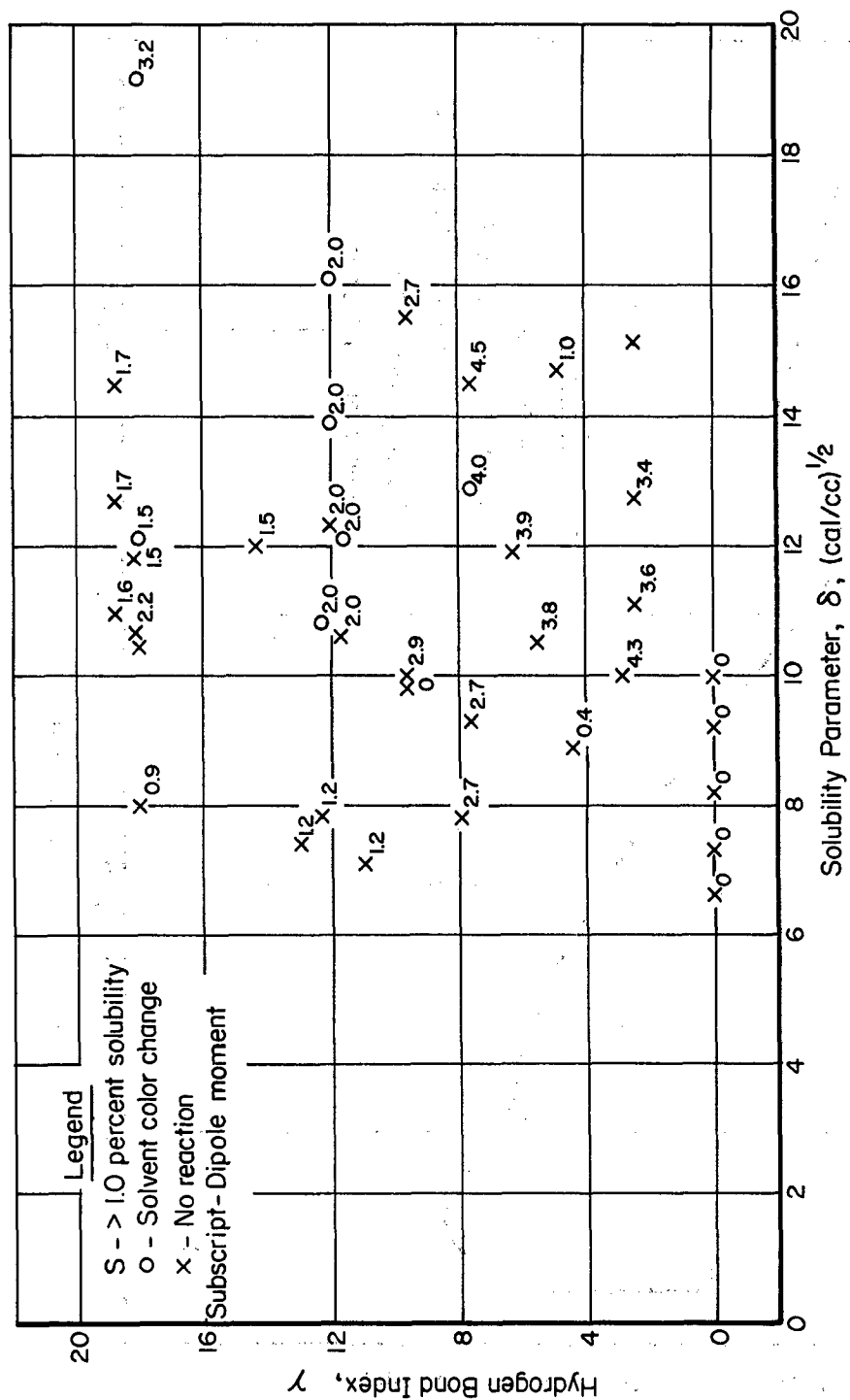


FIGURE 24. SOLVENT FORMULATING MAP FOR POLYPYRROLONE POLYMER
SAMPLE PE-82

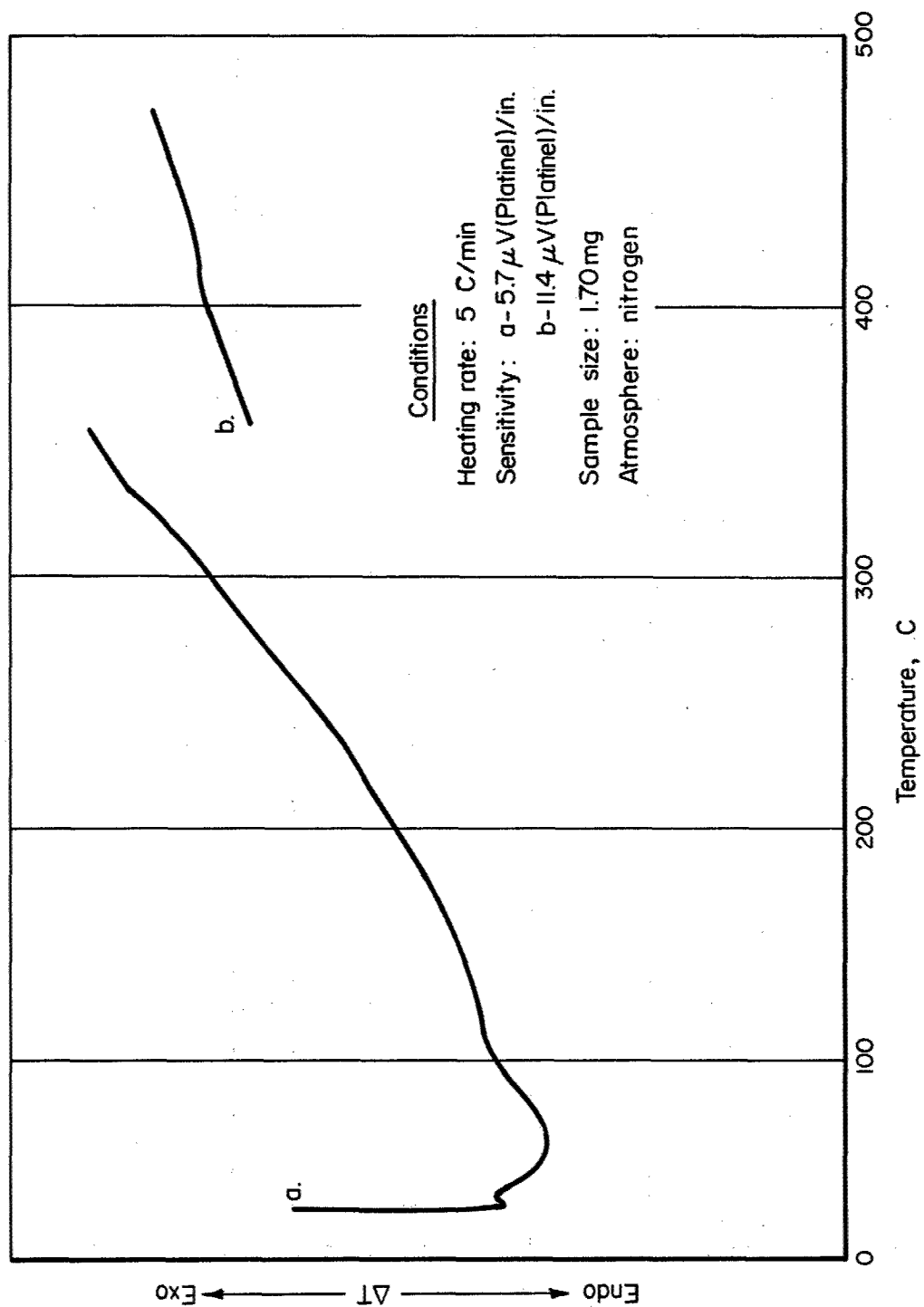


FIGURE 25. DTA THERMOGRAM OF POLYPYRROLONE POLYMER
SAMPLE PE-82

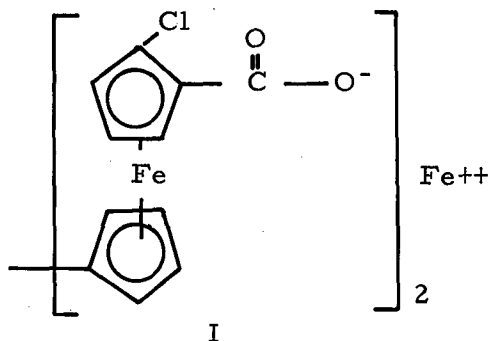
rates of the thermally induced reactions which are occurring do not differ in their temperature dependence.

The TGA thermogram, Figure 26, confirms the conclusions drawn from the DTA thermogram. The initial 1.6 percent weight loss is indicative of loss of absorbed volatiles. The nearly linear loss of weight between 100 and 900 C is consistent with a weight-loss mechanism following several overlapping mechanisms.

The mass spectrometer - TGA combination was used to identify the volatile products evolved during heating of the PE-82 sample. It is clear from the plot of the intensity of the 18 m/e peak as a function of temperature (see Figure 27) that water is evolved by two different mechanisms. It appears likely that the first peak is produced by loss of physically retained water, and the second by cyclodehydration. Evolution of CO₂ from this sample suggests decarboxylation is occurring in addition to cyclodehydration. Since cyclodehydration decreases the concentration of acid groups, the observed decrease in rate of evolution of CO₂ at high temperatures would be expected. Any decarboxylation that occurs will prevent cyclodehydration and therefore result in ladder defects. In addition, the removal of acid groups will increase the probability of intermolecular reactions involving loss of water.

Ferrocenylene Sample

A sample of the product obtained by heating 1-carboxy-2-chloroferrocene, labelled 48133-29-P, was submitted to Battelle for determination of the reaction mechanism to improve polymerization technique and assist polymerization of more highly chlorinated monomers. The elemental analysis listed in Table VIII was obtained from Schwarzkopf Analytical Laboratory. It is in better agreement with Structure I than with Structure II,



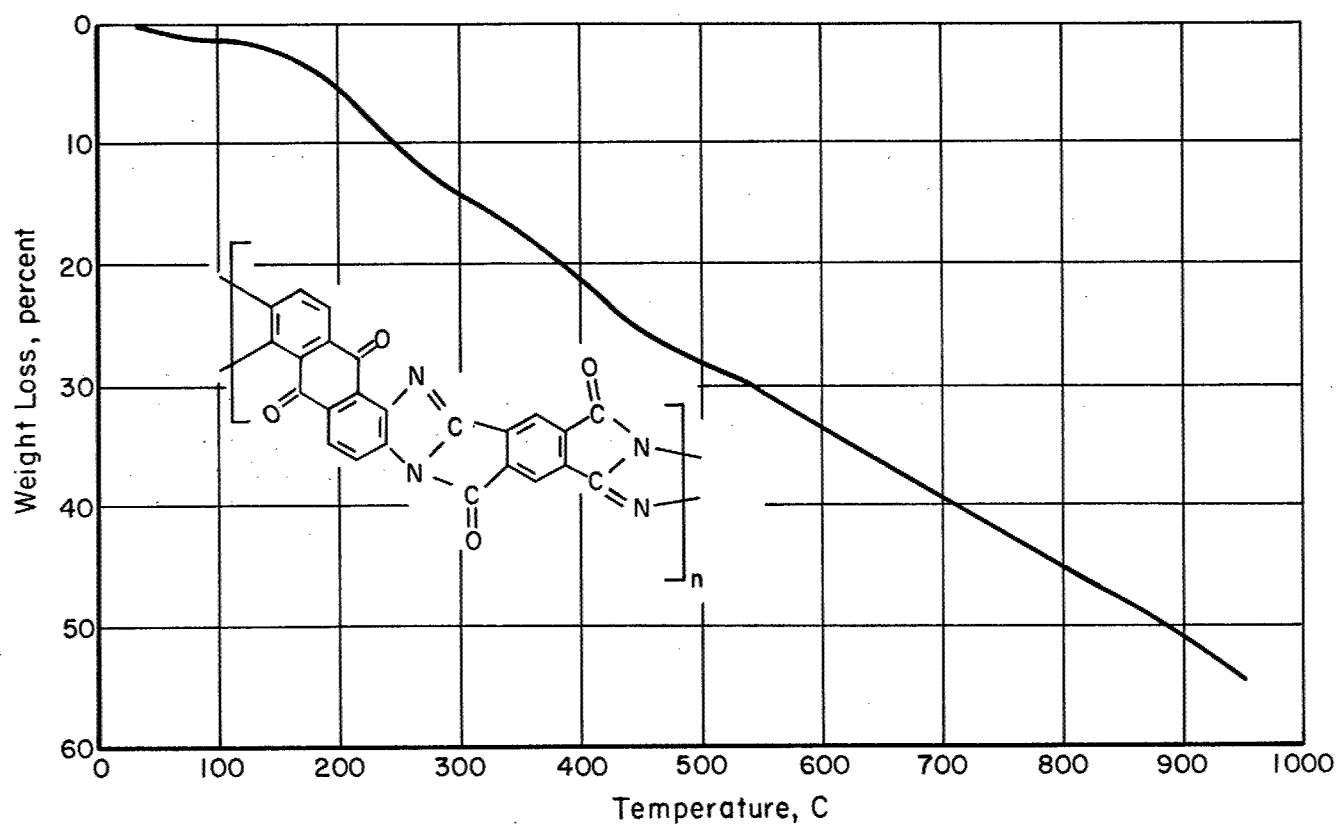


FIGURE 26. TGA THERMOGRAM OF POLYPYRROLONE POLYMER SAMPLE PE-82 AT 4 C/MIN HEATING RATE AND 0.1 TORR USING A 9.40 MG SAMPLE

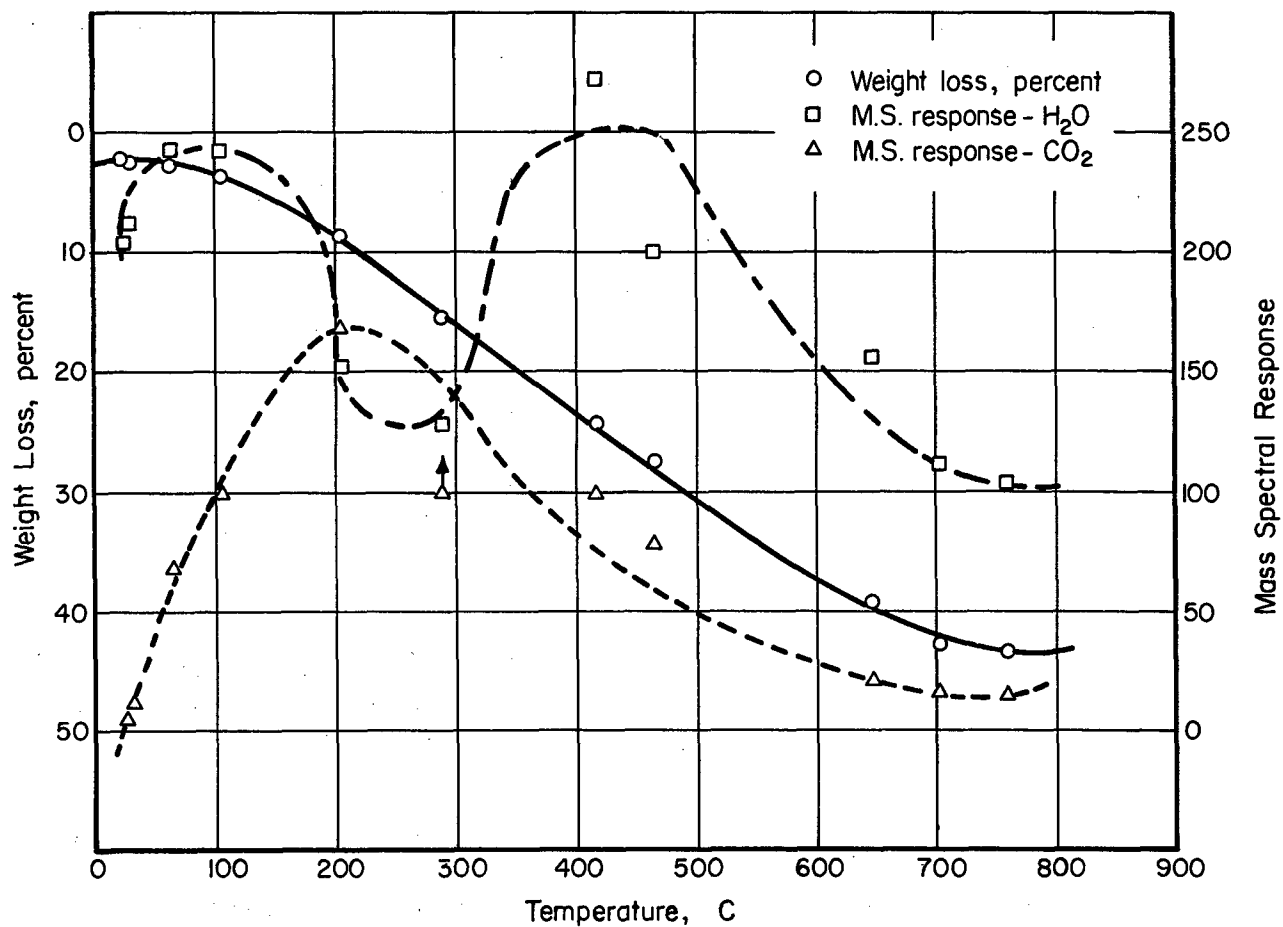
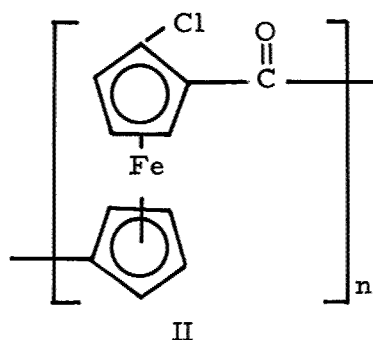


FIGURE 27. DEPENDENCE ON TEMPERATURE OF THE VOLATILES PRODUCED BY HEATING POLYPYRROLONE POLYMER SAMPLE PE-82



although it is difficult to rationalize a mechanism by which Structure I would be produced.

TABLE VIII. ELEMENTAL ANALYSIS OF FERROCENYLENE
SAMPLE 48133-29-P

Element	Analysis, percent		Found(a)
	Calculated		
	Structure I	Structure II	
C	45.56	53.60	46.79
H	2.41	2.84	3.26
Cl	12.08	14.41	15.82
Fe	28.89	22.65	26.10
O	11.05	6.50	8.03(b)

(a) Average from duplicate analysis.

(b) By difference.

The infrared spectrum of the product was examined as a first step toward identification of the reaction mechanism. The spectrum (see Figure 28) contains large bands and broad nondistinctive bands in the $1620\text{-}1300\text{ cm}^{-1}$ region characteristic of an oxidized mixture.

Since analysis of the structures of the product was not fruitful for elucidating the reaction mechanism, identification of the volatiles produced by the reaction was undertaken. A sample of the "monomer" (1-carboxy-2-chloroferrocene prepared by F. Hedberg, AFML) was examined by DTA to identify a temperature suitable for carrying out the reaction. The thermogram (see Figure 29) indicates melting at 178 C and an exothermal process starting at a temperature just above melting. The exothermal process was over by the time the sample reached 230 C , suggesting that the reaction rate is appreciable below this temperature.

A programmed TGA obtained on the monomer at 0.1 torr indicated 75 percent weight loss by 150 C . Therefore, the reaction occurring at temperatures greater than 180 C could not be run under vacuum on the TGA balance as required to continuously monitor the evolved products with the mass spectrometer (Battelle's AEI MS-10). When heated at atmospheric pressure under N_2 , the sample lost 35 percent by weight between 175 and 250 C . After completion of the programmed heating, the atmosphere of the TGA system was introduced into the MS-10 through a variable leak valve. No significant peaks

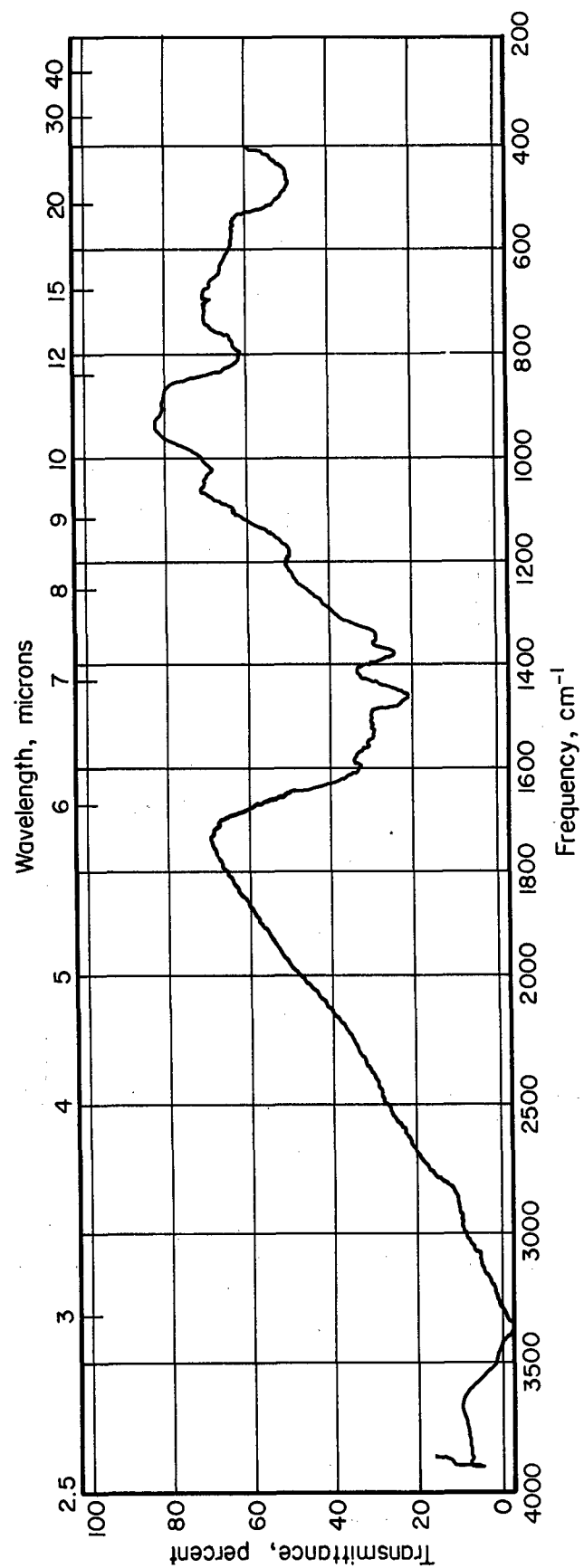


FIGURE 28. INFRARED SPECTRUM OF FERROCENYLENE SAMPLE 48133-29-P

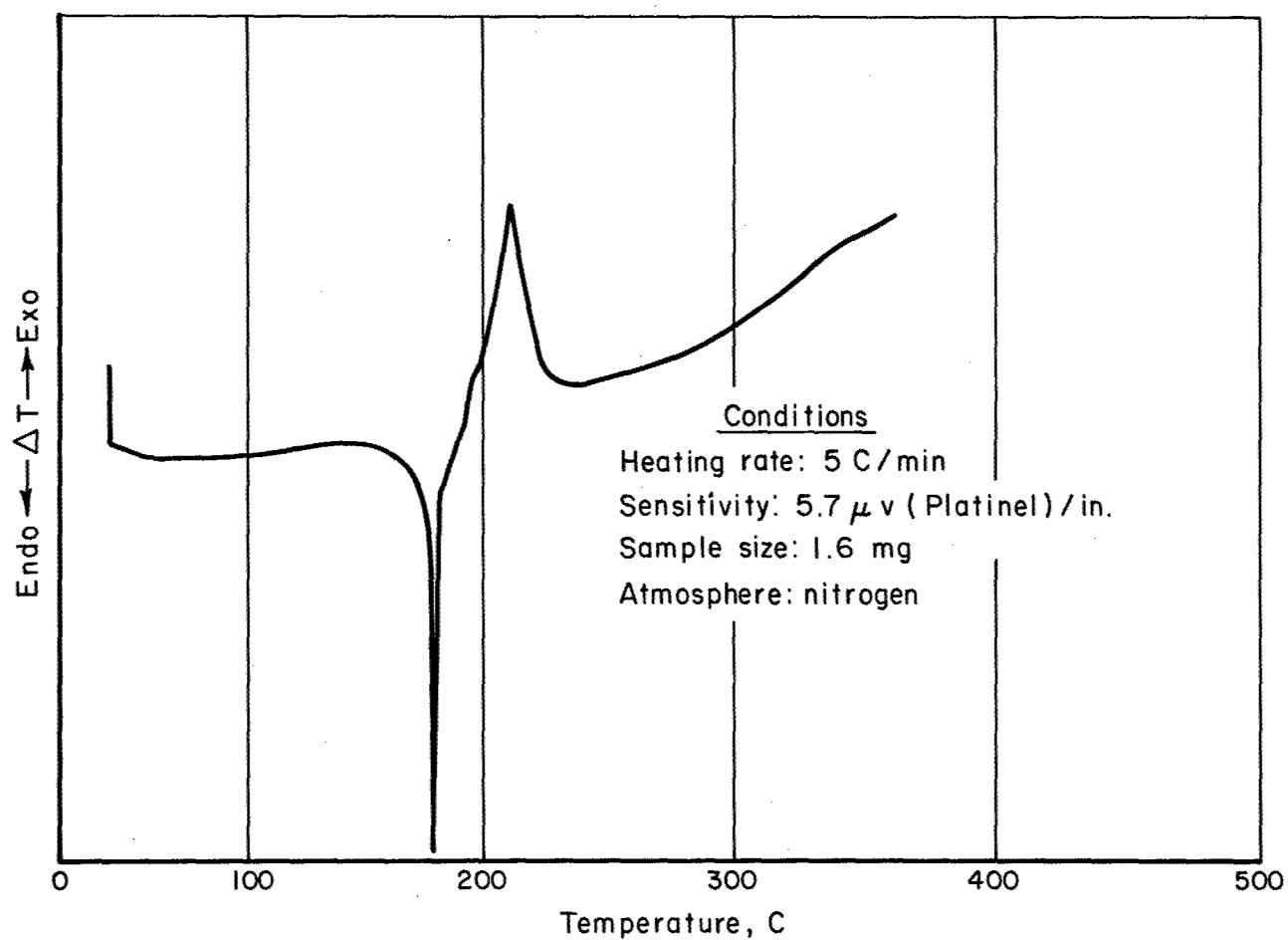


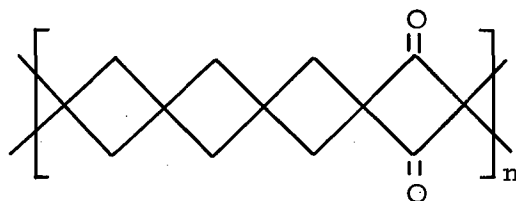
FIGURE 29. DTA THERMOGRAM OF 1-CARBOXY-2-CHLOROFERROCENE SAMPLE 48133-29

were detected, possibly, as a result of absorption of the evolved products on the walls of the TGA hangdown tube. While loss of Cl and CO₂ from each "monomer" unit would produce a 30 percent weight loss, the elemental analysis given in Table IX is inconsistent with this.

In an effort to reduce the difficulties encountered with identification of the volatile products by TGA-mass spectrometry, the reaction was carried out in a glass U-tube. The U-tube was connected to a specially designed trap (for description see Reference 2) to permit collection of the volatiles from the reaction before analysis. Nitrogen was bled through the U-tube during the reaction to sweep the volatiles into the trap, which was maintained at liquid-nitrogen temperature. The time required to reach the reaction temperature was minimized by preheating a silicone oil bath to the desired temperature before inserting the U-tube with the sample in the bath. The components collected in the trap were separated by gas chromatography (GC) using a Porapak QS column. They were tentatively identified by comparison of their retention times with those of expected products of the reaction. This analysis indicated that H₂O and CO₂ were produced in a ratio of approximately 16:1. Several other peaks were also observed. Of these, only a peak with retention time close to water was present in appreciable amounts. These results suggest that the predominant reaction is formation of anhydride with some decarboxylation. However, if one assumes that these are the only reactions occurring, neither the reported elemental analysis nor the sample insolubility would be explained. Therefore, it appears likely that thermal breakdown of the ferrocene moiety also occurs. It is planned to use high-resolution mass spectrometry to identify the additional components observed in the GC trace. Hopefully, these will include cyclopentadiene and its fragments. In addition, it is planned to conduct the reaction in solution at less than 180 C in an effort to reduce the extent of reaction.

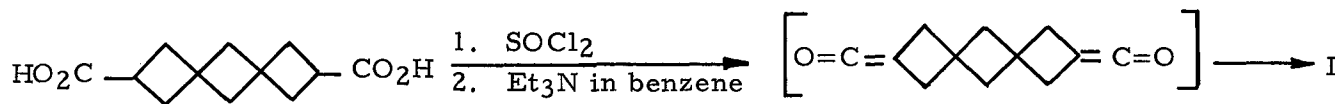
Polyspirocyclobutane Polymers

Samples of this class, labelled 83A and 83B, which are expected to have the structure



I

were received for characterization. They were prepared by C. M. Sharts and coworkers by the general reaction⁽¹¹⁾



The molecules are expected to be terminated with carboxyl groups. The IR spectra of these samples were included in the transmittal information. In these spectra, that of Sample 83A had no detectable absorption in the carboxyl carbonyl region, while that of Sample 83B had considerable absorption in the carboxyl carbonyl region. These results suggest that Sample 83A is closer to the proposed structure. Therefore, 83A was chosen as representative of structures of this type, and is being thoroughly characterized at Battelle.

Elemental analysis of these samples, shown in Table IX is in poor agreement with the proposed structure. Clark reports Sample 83A was "uncontrollably explosive, without melting", which obviously made analysis difficult. However, the difference between the observed and calculated result far exceeds the estimated standard deviation of the measurement. It is interesting that IR spectrometry indicates structural differences between these samples which are not confirmed by the elemental analysis.

TABLE IX. ELEMENTAL ANALYSIS OF THE POLY-(TRISPIRO[3.1.1.3.1.1] TRIDECANE-1,3-DIONE) SAMPLES 83A AND 83B

Element	Analysis, percent		
	Calculated	Found(a)	
		83A	83B
C	78.00	73.95 \pm 0.40(b)	74.55
H	6.00	6.87 \pm 0.21(b)	7.76
O	16.00	19.18(c)	17.69(c)

(a) Clark Microanalytical Laboratories.

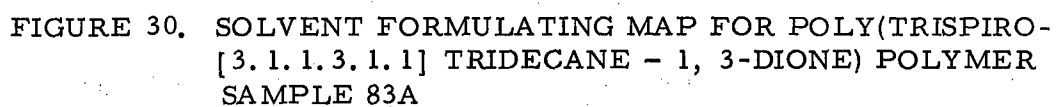
(b) Average and estimated standard deviation of five measurements.

(c) By difference.

A solvent search with Sample 83A, using the microscopic technique⁽¹⁾ and the solvents listed in Table IX, indicated solubility to greater than 0.10 percent in pyridine and aniline. The sample was partially soluble in hexamethylphosphoramide (HMP) and N,N-dimethylaniline. The combination of solvent properties where solution formation is favored for this sample is shown in Figure 30.

A solvent search with Sample 83B using the same technique and solvents as for Sample 83A indicated solubility in many basic solvents. These include HMP, pyridine, aniline, DMF, DMAC, DMSO, as well as all nitrogen-substituted formamides and acetamides. The solubility of Sample 83B in basic solvents gives additional support to the presence of carboxyl groups. The solvent formulating map for this sample is shown in Figure 31.

The TGA thermogram of Sample 83A, Figure 32, indicates that this sample does not have good thermal stability. The shape of the thermogram suggests that the weight loss observed at 200 C is occurring by the same mechanism as that at the higher temperatures. If this is the case, the upper service temperature of materials with this structure would be below 200 C.



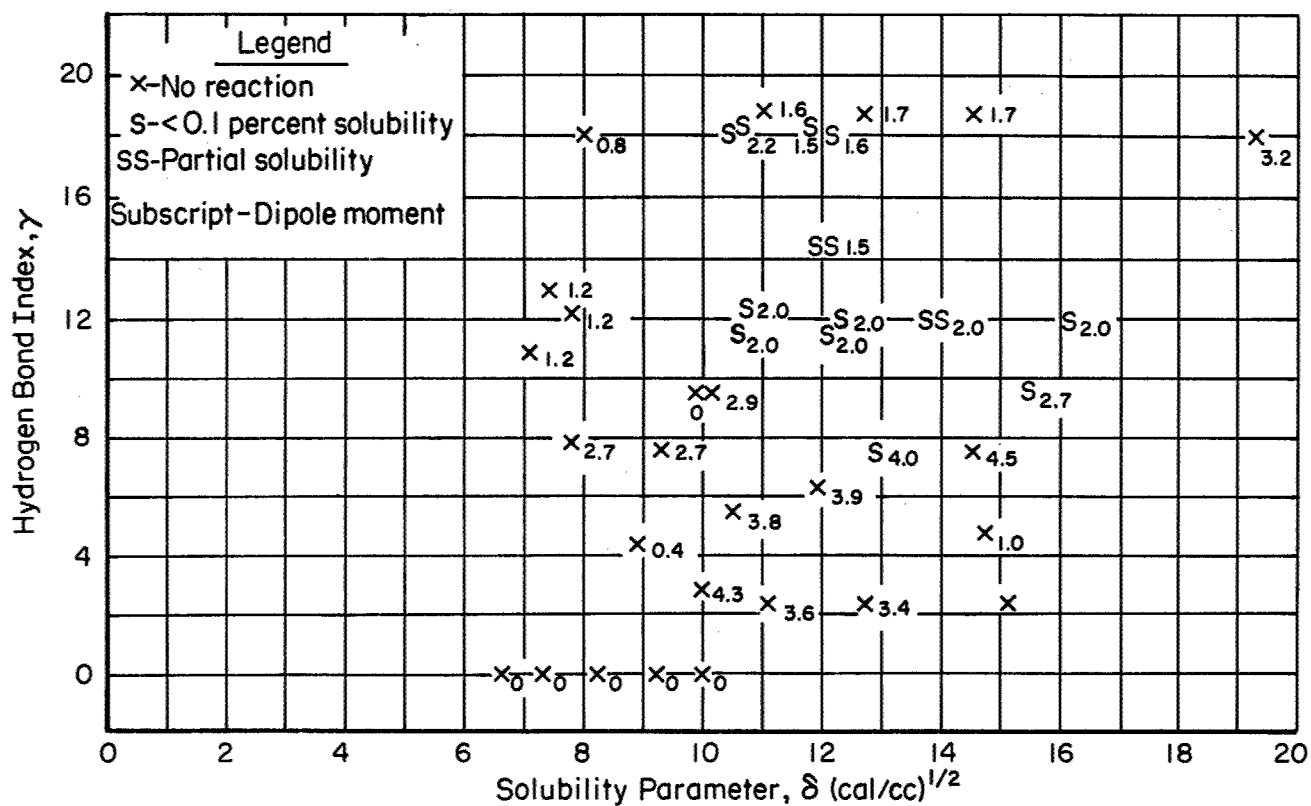


FIGURE 31. SOLVENT FORMULATING MAP FOR POLY(TRISPIRO-[3.1.1.3.1.1] TRIDECANE-1,3-DIONE) POLYMER
SAMPLE 83 B

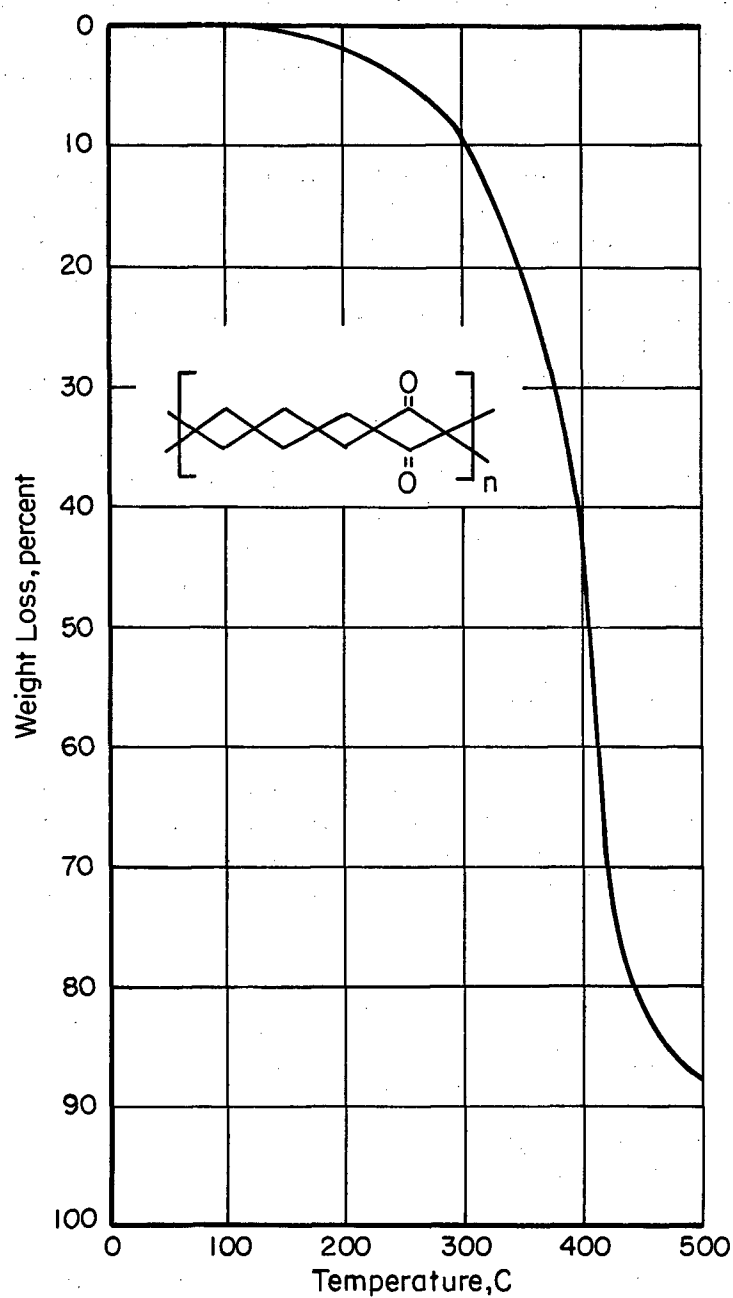


FIGURE 32. TGA THERMOGRAM OF POLY(TRISPIRO[3.1.1.3.1.1]-TRIDECANE - 1,3-DIONE) POLYMER SAMPLE 83A AT 4 C/MIN HEATING RATE AND 0.1 TORR USING A 1.10 MG SAMPLE

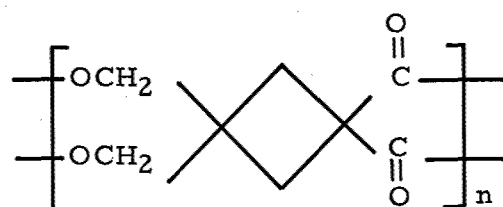
The DTA thermogram of Sample 83A (Figure 33) exhibited no definitive endotherm attributable to solvent loss and no enthalpic peaks other than the broad exothermal peak at 400 C corresponding to the maximum rate of weight loss in the TGA thermogram. The DTA thermogram was obtained on Battelle's new R. L. Stone DTA, which has sub-ambient capabilities. The heating rate used in this analysis was 5 C/min as compared with the 4 C/min used previously. This difference is unlikely to appreciably affect the shape of the DTA thermogram. Although heating rate can be continuously varied between 0.5 C/min and 50 C/min, 4 C/min is not a convenient set position on this instrument.

In an effort to elucidate the breakdown mechanism of Sample 83A, the source of the weight loss of the sample was examined using the TGA-MS10 combination. By 100 C, an m/e peak at 44 was observed, suggesting loss of CO₂. In addition, peaks attributable to residual SOCl₂ were detected. By 250 C, the peaks which were observed were so numerous that identification of the thermal fragments became extremely difficult. GC separation of the thermal fragments before introduction into the mass spectrometer appears to be the best approach to identification of fragmentation products of this sample.

The IR spectrum of Sample 83A (see Figure 34) shows a strong carbonyl band at 1735 cm⁻¹, an absorption expected for an aliphatic ester or ketone attached to a strained (less than 6 carbon) ring. There is no evidence for a ketone group or acid carbonyl. A shoulder on the carbonyl band at about 1710 cm⁻¹ could be from residual acid.

Diethyl-3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate Polymers

Samples expected to be spiropolyesters (labelled DLS-30 and DLS-31), which were prepared by heating diethyl-3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate⁽¹²⁾, were received for characterization. Sample DLS-30 was prepared in the presence of antimony(III) oxide and calcium acetate dihydrate, while DLS-31 was not. The proposed structure is



These samples were transmitted to Battelle in glass crystallization dishes. Separation of the samples from the glass was made difficult by the strong adhesion of the polymer to the glass, and the shattered state of the dishes.

Elemental analysis of the samples, shown in Table X, are in fairly good agreement with the proposed structure. The results in the table are corrected for ash content, which was attributed to residual glass chips.

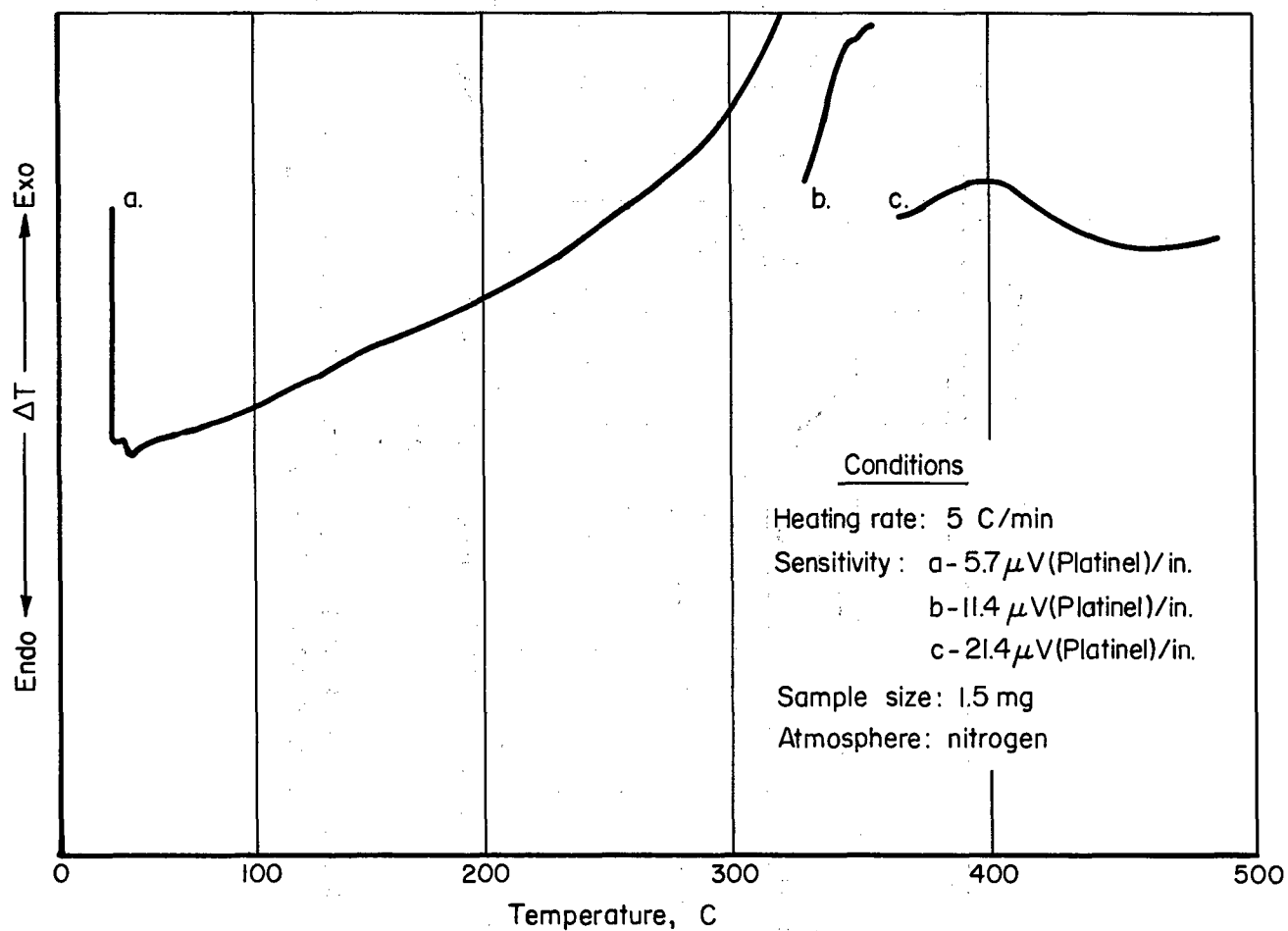


FIGURE 33. DTA THERMOGRAM OF POLY(TRISPIRO[3.1.1.3.1.1]-TRIDECA-1,3-DIONE) POLYMER SAMPLE 83A

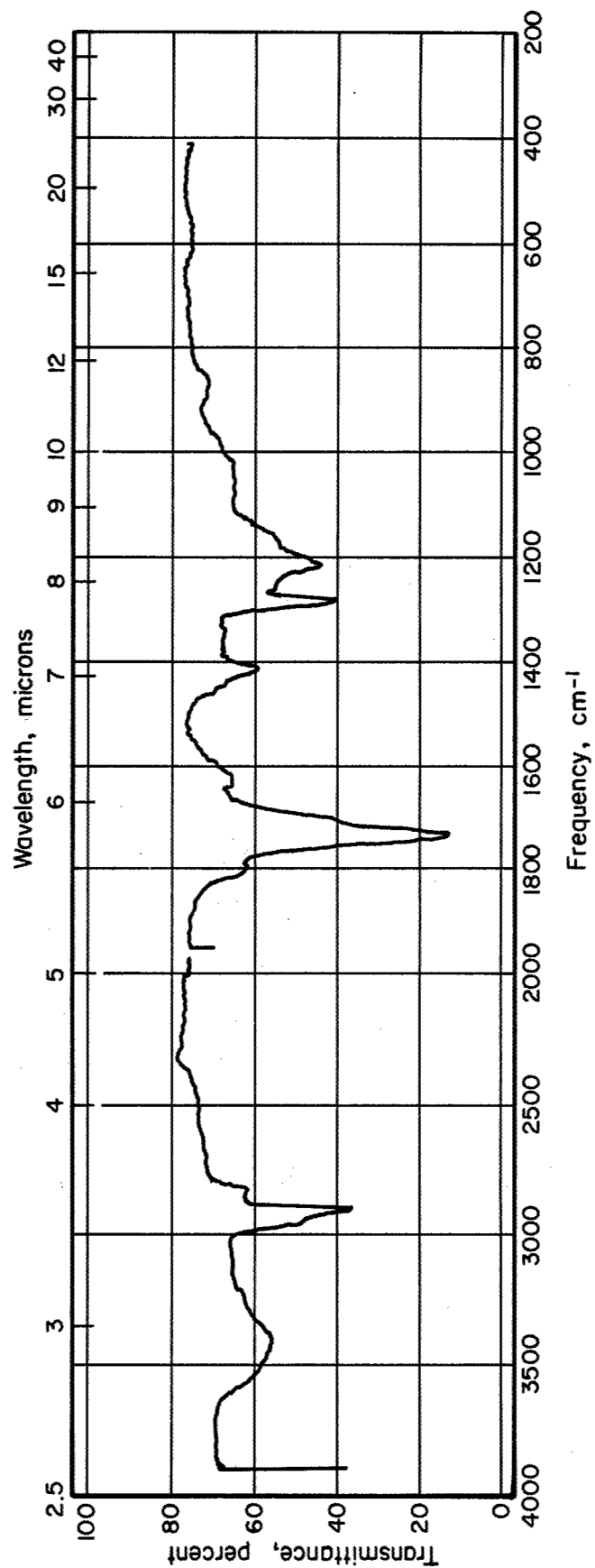


FIGURE 34. INFRARED SPECTRUM OF POLY(TRISPIRO[3.1.1.3.1.1]-TRIDECANE-1,3-DIONE) POLYMER SAMPLE 83A

TABLE X. ELEMENTAL ANALYSIS OF DIETHYL 3, 3-BIS (HYDROXYMETHYL)CYCLOBUTANE-1, 1-DICARBOXYLATE SAMPLES DLS-30 AND DLS-31

Element	Calculated	Analysis, percent	
		Found(a)	
		DLS-30	DLS-31
C	57.14	58.07	58.05
H	4.76	5.79	5.64
O	38.10	36.44	36.31

(a) Clark Microanalytical Laboratories - average of two runs.

A solvent search using the microscopic technique⁽¹⁾ did not indicate complete solubility in any solvent. However, both samples interacted slightly with diethylformamide, dimethylformamide, dimethylacetamide, N-ethylacetamide, and aniline. The solvent formulating map for these samples, Figure 35, was generated with solvents listed in Table IV.

Solvent Search

The solubility parameter approach to prediction of solution formation proposed by Hildebrand and Scott⁽¹³⁾ employs the square root of the ratio of the heat of vaporization (E_{vap}) and molar volume (\bar{V}) of the solution components to calculate their heat of mixing. This approach has presented major problems when dealing with mixtures where interactions other than dispersion forces are possible. Since situations of this type predominate when dealing with the new high-temperature polymers, there is considerable incentive for developing means for dealing with them. The difficulty has been attributed to incomplete description of the nature of the solvents by $(E_{\text{vap}}/\bar{V})^{1/2}$ although it could also arise from neglect of the entropy of solution implicitly included in the solubility-parameter approach. Substantial improvement in the reliability of prediction was attained by qualitative⁽¹⁴⁾ and later quantitative^(9, 15) addition of a measure of the H-bonding tendency of the solvent. Additional benefit was derived by addition of the dipole moment as a solvent parameter affecting solution formation. Crowley et al. ⁽⁹⁾, cite considerable solubility data on a few polymers, suggesting that these modifications improve the reliability of prediction of solution formation.

The recent work of Drago⁽¹⁶⁾ provides conclusive evidence that there is an inherent error in use of the solubility parameter calculated by the Scott and Hildebrand method when dealing with potentially interacting solvents. His results unequivocally demonstrate that in Lewis acid-base reactions, the relative strength of the acid (or base) depends on the structure of the base (or acid) with which it interacts. Only if the intermolecular forces have at least two independent components can his results be explained. Drago has assumed that the independent forces can be lumped into electrostatic and covalent contributions. Electrostatic forces arise from dipole-dipole, dipole-induced dipole, and H-bonding interactions while covalent forces arise from London dispersion interactions. Drago further assumes that the enthalpy of formation of an acid-base adduct can be written as

$$\Delta H = E_A E_B + C_A C_B \quad (1)$$

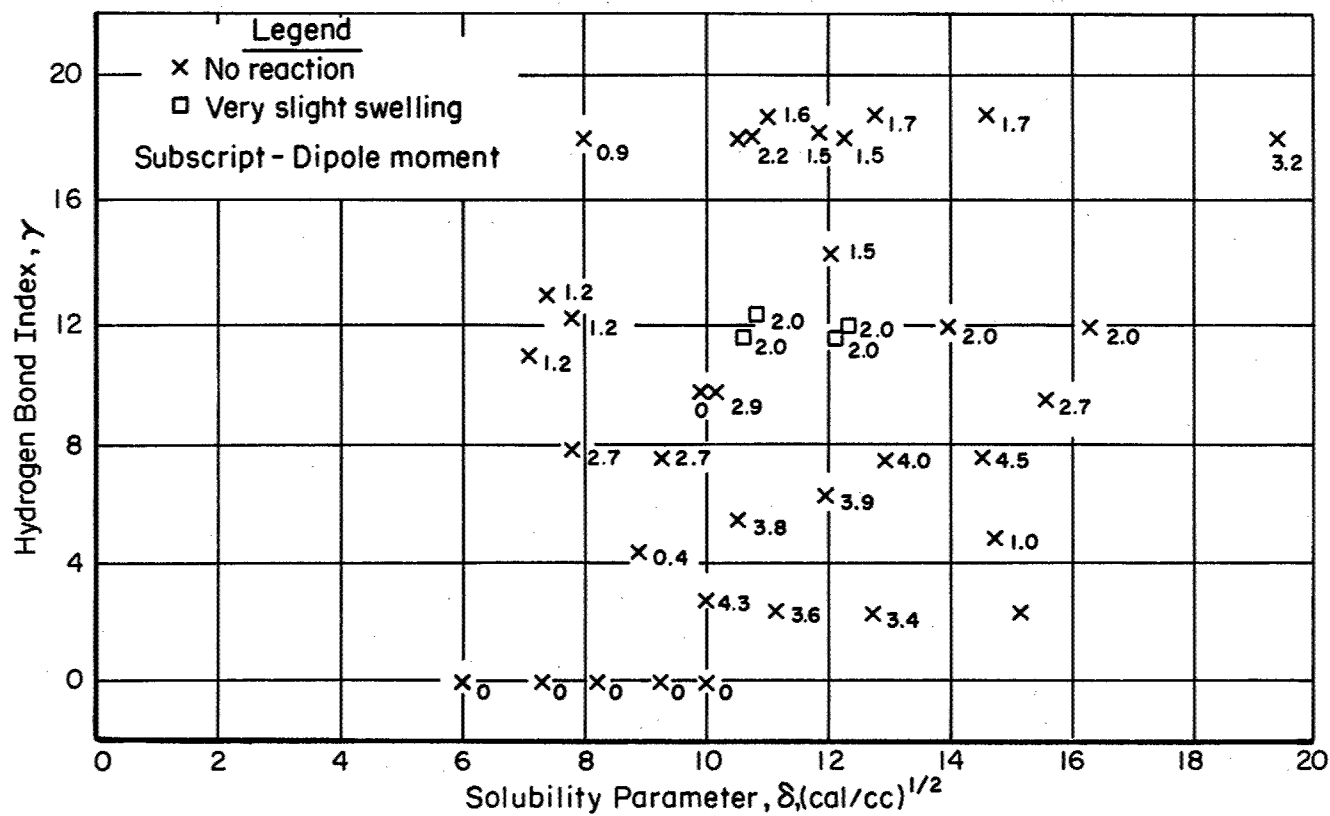


FIGURE 35. SOLVENT FORMULATING MAP FOR DIETHYL 3,3-BIS-(HYDROXYMETHYL)CYCLOBUTANE-1,1-DICARBOXYL-ATE POLYMER SAMPLES DLS-30 AND DLS-31

where the E and C terms, respectively, are the electrostatic and covalent character of the acid and base. By using experimentally determined ΔH values (either reported in the literature, or found in his laboratory) for approximately 160 adducts, Drago calculated a set of self-consistent E and C values by assuming $E_A = C_A = 1$ for the acid I_2 . The mean error between the calculated and experimentally measured values of ΔH was less than 2.5 percent, a very surprising result in view of the difficulty in measuring ΔH unperturbed by solvent effects.

In describing a solvent as a Lewis acid (or base), one is referring to the electron-accepting (or -donating) power of the solvent. Since all solvents can be classified in this manner (usually in both classes), prediction of ΔH of formation of a solvent by Equation (1) appears appropriate, particularly in view of the range of electron-donor strength included in Drago's investigation. Support for this contention is provided by Bondi and Simken⁽¹⁷⁾, who accurately predicted heats of vaporization (ΔE_{vap}) by hydroxylated compounds by dividing intermolecular forces into polar and nonpolar components.

The fundamental thermodynamic relation for the free-energy change produced by mixing solvent and solute, i. e. ,

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad , \quad (2)$$

indicates that a small positive ΔH_m or a negative value of ΔH_m and a large positive ΔS_m favors solution formation. Generally, it can be assumed that the magnitude of ΔS_m for polymers mixed with low molecular weight solvents is not particularly solvent dependent. Therefore, approaches to prediction of solution formation have focused on determining the magnitude of ΔH_m , defined by the relation

$$\Delta H_m = \Delta H_{11} + \Delta H_{22} - \Delta H_{12} \quad , \quad (3)$$

where ΔH_{ij} is the enthalpy of formation of the i-j adduct. Clearly, ΔH_m is minimized when ΔH_{12} is greatest. If the form of Equation (1) is appropriate for description of intermolecular forces in a solvent, it can be shown that ΔH_{12} is greatest when the electrostatic and covalent character of species 1 is equal to that of species 2. Prediction of ΔH_{12} from the geometric mean of ΔH_{11} and ΔH_{22} , the approach used by previously cited workers⁽⁷⁻¹⁰⁾, is seriously in error if the electrostatic or covalent character of species 1 differs appreciably from that of species 2. These arguments strongly suggest that the divided solubility parameter should be used in solvent searches. This approach is only practical, however, if a means for accurately predicting the covalent and electrostatic character of a large number of solvents from existing (or readily obtainable) data can be developed.

It has been suggested⁽¹⁷⁻¹⁹⁾ that the contribution to ΔE_{vap} of covalent (or dispersion) forces in polar solvents can be estimated from the ΔE_{vap} of their homomorph.⁽²⁰⁾ A homomorph of a solvent is the saturated hydrocarbon with analagous structure. The electrostatic (or polar) contribution is taken as the difference between the heats of vaporization of the homomorph and the solvent. Recently, Hansen⁽¹⁹⁾ has suggested that H-bonding should be considered separately from the other forces contributing to the electrostatic energy. While his suggestion has merit, techniques for separating these effects are laborious and inaccurate.

We have used Hansen's data⁽¹⁹⁾ to develop a list of solvents which provide as complete coverage of solvent properties as possible with available solvents. The

coverage attained is illustrated by the solvent formulating map given in Figure 36. While some regions of the map are not covered, the absence of any solvent with properties in these regions makes it doubtful that polymers with such properties exist. Of course, some of the spaces could be filled by mixing solvents and using the rule of moments for calculating the solubility parameters of the mixture. The solvents used to form the solvent formulating map and their pertinent properties are listed in Table XI.

The effect of division of the solubility parameter into electrostatic and covalent portions on coherency of the region of solubility for polymers examined in this program is illustrated by comparison of solvent formulating maps generated by this approach with those generated by the approach previously described⁽²⁾. Figure 37 is the solvent formulating map for the poly(perfluoro-alkylperfluoroalkylenetriazine) BT-21. Apparent inconsistencies occur at $\delta = 12.0$, $\gamma = 18.0$, and $\delta = 10.0$, $\gamma = 9.7$. When the solubility parameter of these solvents is divided into the dispersion (covalent) and polar (electrostatic) portion, the inconsistencies in the region of solubility are removed (see Figure 38). The identified points in Figure 38 were the ones that overlapped in Figure 37. Comparison of the region of solubility in Figures 39 and 40 provided further evidence that the divided solubility parameter approach results in a more coherent region of solubility. In Figure 39, the range between 18.0 and 18.7 includes alcohols that are not solvents and basic solvents which dissolve the polymer. Also, as was the case for the BT-21 sample, acetone and dioxane differ in their solution forming properties with the sample although they have similar H-bonding and solubility parameters ($\delta = 10.0$, $\gamma = 9.7$). Both of these inconsistencies are absent in Figure 37, where the divided solubility parameters have been used. An apparent inconsistency is present in Figure 40 which was not present in Figure 39. Formic acid dissolved the sample although it is outside the solution-forming region. However, the polymer, a sample of poly(2,4-diaminotoluene bibenzoxazole), has several basic sites which make it probable that it exists in formic acid as a protonated species. Since a protonated species would be expected to have electrostatic properties different from the unprotonated species, it is not surprising that dissolution occurs in a solvent with properties outside the solubility region where the unprotonated species dissolves. If this postulate is correct, introduction of a protonated species into solvents with electrostatic and covalent solubility parameter components similar to formic acid would be expected to produce solution. After addition of a small amount of HCl to a mixture of the sample with methanol and ethylene glycol which were nonsolvents for the unprotonated species, solution formation occurred. Although ethanol is in the same region of the solvent map, dissolution was not observed. It is believed that the dielectric constant of ethanol is too low to permit appreciable concentration of the dissociated protonated species which is soluble in solvents with these properties.

TABLE XI. SOLVENTS FOR USE IN SOLVENT SEARCH AND
PERTINENT PROPERTIES

Solvent	Literature Boiling Point, C	Solubility Parameters, $\left(\frac{\text{cal}}{\text{cc}}\right)^{1/2}$	
		δ_a	δ_d
Carbon disulfide	46	0	9.97
Carbon tetrachloride	77	0	8.65
Cyclohexane	81	0	8.18
n-Hexane	69	0	7.24
Benzene	80	1.48	9.03
Tetralin	207	1.5	9.4
Dipropylamine	111	2.13	7.50
Toluene	110	2.18	8.67
Isopropylbenzene	152	2.50	8.15
Diisobutylketone	168	2.64	7.77
Diethylether	35	2.65	7.05
o-Dichlorobenzene	180-3	2.95	9.43
Diethylamine	56	3.18	7.30
Sym-Tetrachloroethane	146	3.58	9.15
o-Xylene	144	3.60	8.22
N, N-Dimethylaniline	193	3.99	8.67
Diisobutylcarbinol	172-4	4.55	7.38
Mesityl oxide	129	4.59	7.97
1,4-Dioxane	101	4.65	8.55
Methylethylketone	80	5.06	7.77
Pyridine	116	5.18	9.25
Aniline	184	5.59	9.53
Nitrobenzene	211	5.72	8.95
Dichlorodiethylether	178	5.98	8.42
Butyronitrile	118	6.00	7.96
Acetone	56	6.13	7.58
Cyclohexanol	161.5	6.93	8.50
n-pentanol	138	7.17	7.81
Nitroethane	115	7.57	8.11
Benzyl alcohol	205	7.85	9.04
2-Propanol	82	8.57	7.70
Dimethylformamide	153	8.69	8.52
Dimethylsulfoxide	189	8.77	9.42
γ -Butyrolactone	206	8.82	9.26
Propylene carbonate	122/17 min	9.00	9.83
Nitromethane	101	9.30	8.03
Formic acid	100	9.65	7.47
Ethanol	78	10.45	7.73
Ethylene carbonate	244	10.50	10.85
1,3-Butanediol	204	11.60	8.10
Methanol	65	12.40	7.42
Ethanolamine	172	12.90	8.35
Dipropylene glycol	229	13.35	7.77
Ethylene glycol	197	14.02	8.25

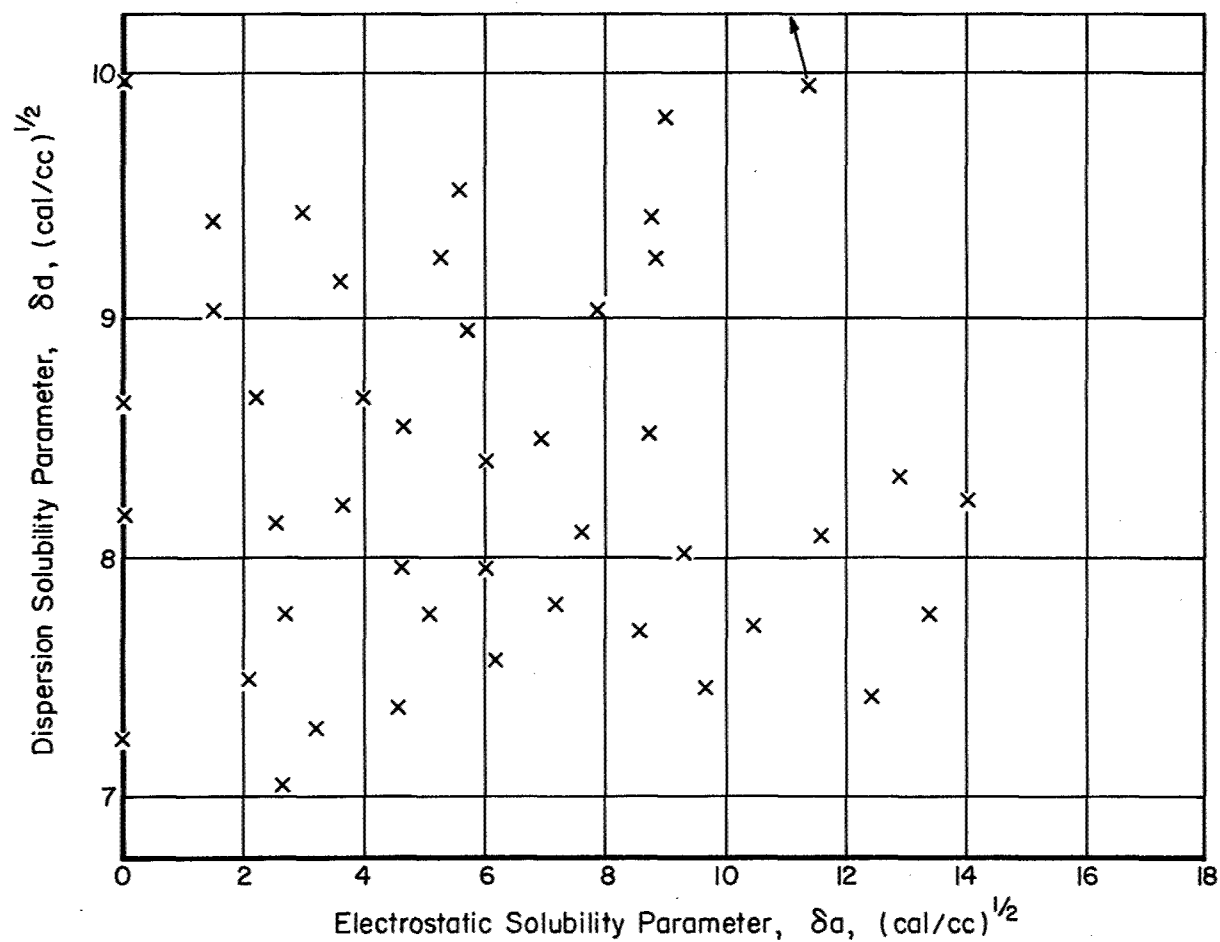


FIGURE 36. SOLVENT FORMULATING MAP WITH DIVIDED SOLUBILITY PARAMETERS

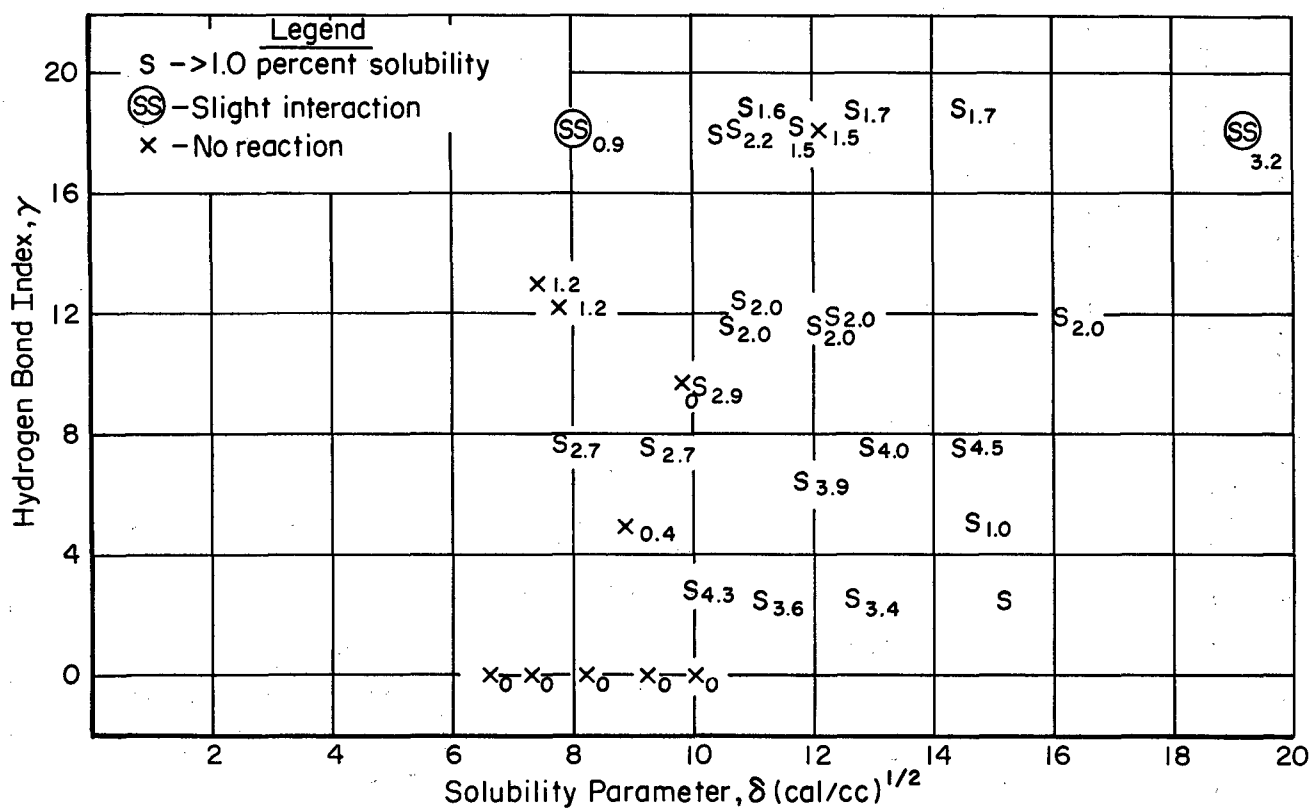


FIGURE 37. SOLVENT FORMULATING MAP FOR POLY (PERFLUOROALKYLENETRIAZINE) POLYMER SAMPLE BT-21

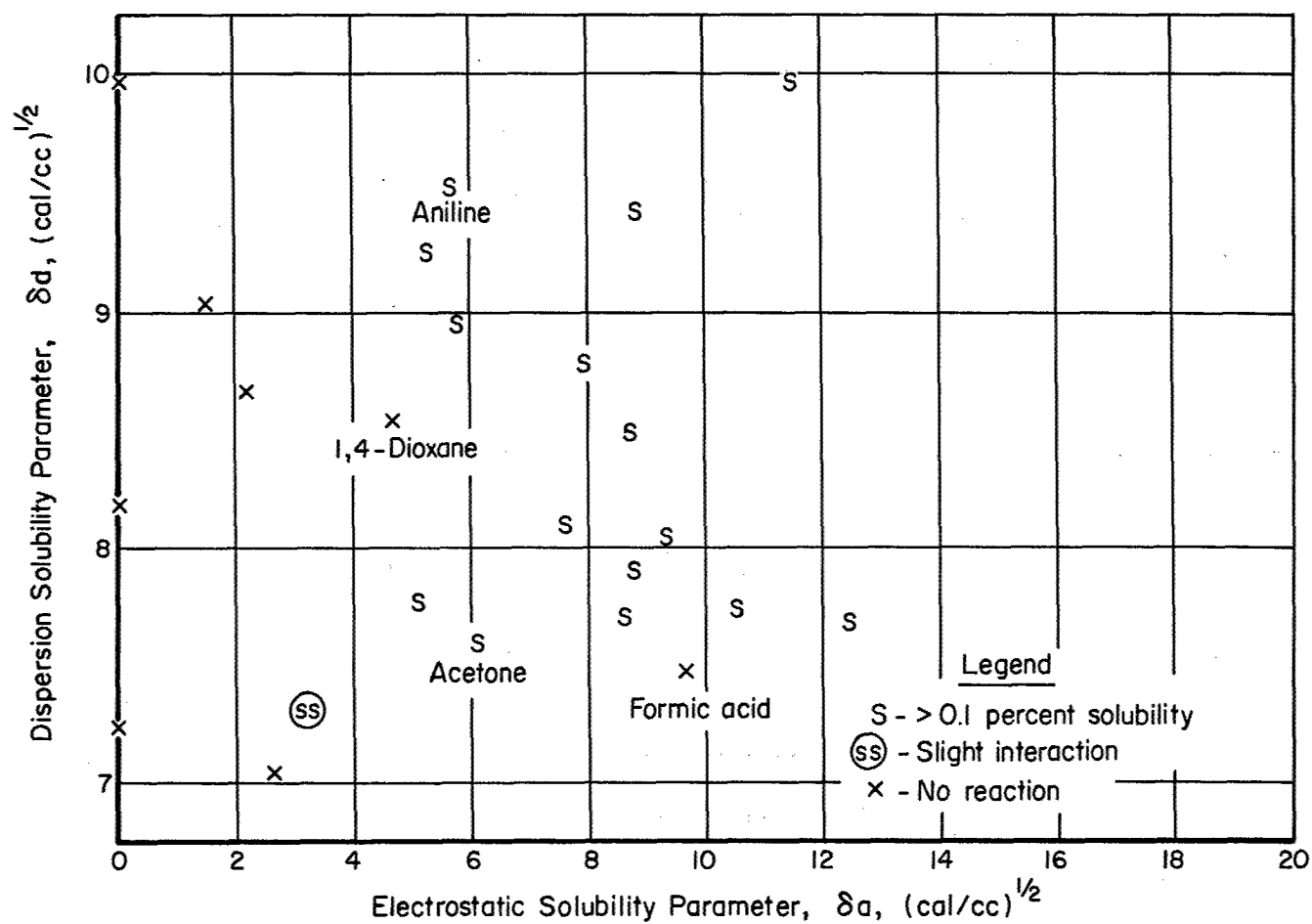


FIGURE 38. REVISED SOLVENT FORMULATING MAP FOR POLY (PERFLUOROALKYLENETRIAZINE) POLYMER SAMPLE BT-21

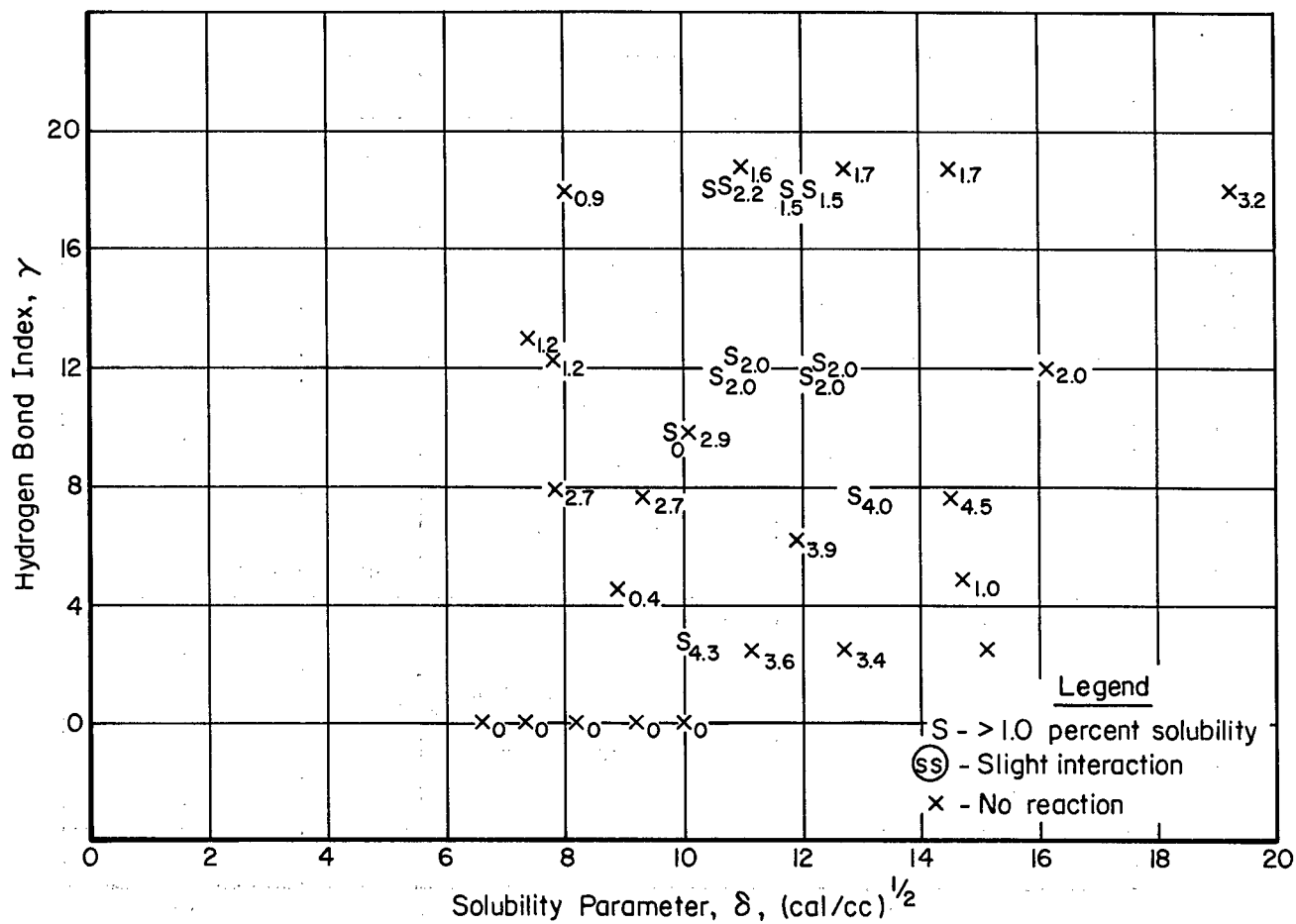


FIGURE 39. SOLVENT FORMULATING MAP FOR POLY (2,4-DIAMINOTOLUENE BIBENZOXAZOLE) POLYMER SAMPLE 48156-22

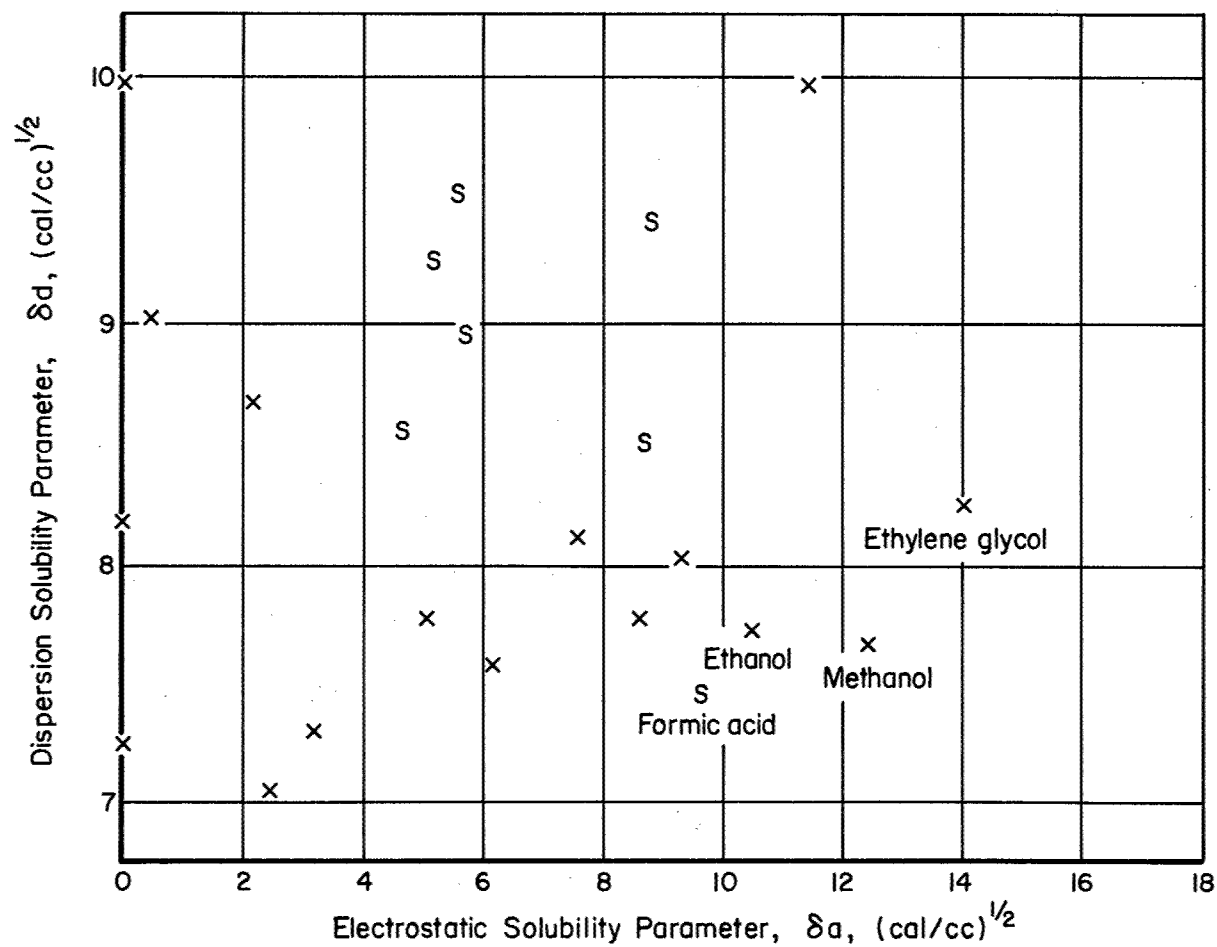


FIGURE 40. REVISED SOLVENT FORMULATING MAP FOR POLY (2,4-DIAMINOTOLUENE BIBENZOXAZOLE) POLYMER SAMPLE 48156-22

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13. ABSTRACT <p>Several samples of a silicon-nitrogen elastomer were characterized. Characterization included structure analysis (elemental composition, IR, and NMR), solubility, solution viscosity, thermal properties (TGA and subambient DTA), and molecular weight (M_n, M_w, GPC distribution). The samples appeared to have the expected structure, i.e., linear polymers, began to volatilize appreciably above 500 C, had a T_g at -27 C, and a broad molecular-weight distribution with M_w as high as 250,000.</p> <p>Several samples of the perfluoroalkyl bibenzoxazole polymers were examined. Considerable effort was directed toward determination of the molecular weight of both perfluorosebacate and perfluoroalkyl ether-linked polymers. In addition, solubility, thermal stability and subambient DTA of the perfluoroalkyl ether-linked polymers (elastomers) were investigated.</p> <p>Samples of the aromatic heterocyclic-ladder type were studied. Mass-spectral identification of the volatiles produced by programmed heating of an incompletely cyclized sample indicated that decarboxylation occurs within the same temperature range as does the cyclization.</p> <p>The product obtained by heating 1-carboxy-2-chloroferrocene was studied. The reaction mechanism was investigated by structural analysis of the product and analysis of the volatiles produced during reaction.</p> <p>Several samples of polyspirocyclobutane polymers were characterized. Characterization includes structural analysis, solubility, and thermal properties.</p> <p>The approach to solvent search was examined in the light of recent literature. It was concluded that division of the solubility parameter into electrostatic and covalent contributions would describe solvent properties pertinent to solution formation. This was supported by examination of solubility data for several polymers.</p> <p>This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Polymer Branch, MANP, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio 45433.</p>			

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